

# **PILOT- AND FULL-SCALE DEMONSTRATION OF ADVANCED MERCURY CONTROL TECHNOLOGIES FOR LIGNITE-FIRED POWER PLANTS**

Quarterly Report

*(for the period of January 1, 2004 – March 31, 2004)*

Prepared for:

AAD Document Control

National Energy Technology Laboratory  
PO Box 10940, MS 921-107  
Pittsburgh, PA 15236-0940

Cooperative Agreement No. DE-FC26-03NT41897  
Performance Monitor: Andrew O’Palko

Prepared by:

Steven A. Benson  
Charlene R. Crocker  
Kevin C. Galbreath  
Jay R. Gunderson  
Michael J. Holmes  
Jason D. Laumb  
Michelle R. Olderbak  
John H. Pavlish  
Li Yan  
Ye Zhuang  
Jill M. Zola

Energy & Environmental Research Center  
University of North Dakota  
Box 9018  
Grand Forks, ND 58202-9018

May 2004

## **DOE DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report is available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

## **ACKNOWLEDGMENT**

This report was prepared with the support of the U.S. Department of Energy (DOE) National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-03NT41897. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors(s) and do not necessarily reflect the views of DOE.

## **EERC DISCLAIMER**

**LEGAL NOTICE** This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by DOE. Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

## TABLE OF CONTENTS

LIST OF FIGURES .....	iii
LIST OF TABLES .....	v
INTRODUCTION .....	1
WORK PLAN .....	1
BACKGROUND .....	2
Mercury Control Options .....	2
Mercury Oxidation .....	5
EXPERIMENTAL .....	7
Objective and Goals .....	7
PLANNED SCOPE OF WORK .....	7
Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs .....	7
Task 2 – Mercury Oxidation Upstream of Wet and Dry Scrubbers .....	8
Task 2.1 – Elemental Mercury Oxidation Additives .....	8
Task 2.2 – Sorbent Injection .....	8
Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation .....	8
Task 3.1 – Impacts of Cofiring on Tire-Derived Fuels .....	8
Task 3.2 – Impacts of Oxidation Catalysts – Coyote Station Slipstream Testing .....	9
Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the <i>Advanced Hybrid™</i> Filter Technology .....	9
Task 5 – Field Testing of Sorbents (revised January 2004) .....	9
RESULTS AND DISCUSSION .....	10
Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs ..	10
Pilot-Scale Facility and Test Plan .....	10
Coal and Combustion Flue Gas Analyses .....	12
Mercury Speciation Across the ESP in the Baseline Test .....	13
Mercury Control Technology Results .....	15
Task 2 – Mercury Oxidation Upstream of Wet and Dry Scrubbers .....	24
Task 2.1 – Elemental Mercury Oxidation Additives .....	25
Task 2.2 – Sorbent Injection .....	25
Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation ..	26
Task 3.1 – Impacts of Cofiring on Tire-Derived Fuels .....	26

Continued . . .

## TABLE OF CONTENTS (continued)

Task 3.2 – Impacts of Oxidation Catalysts – Coyote Station Slipstream Testing .....	26
Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the <i>Advanced Hybrid</i> <sup>TM</sup> Filter Technology .....	26
Advanced Hybrid <sup>TM</sup> Filter Operation .....	27
Mercury Speciation Across the Advanced Hybrid <sup>TM</sup> Filter in Baseline Test.....	28
Mercury Control Technology Results .....	29
Task 5 – Field Testing of Sorbents.....	37
 FUTURE WORK – NEXT QUARTER .....	 39
REFERENCES .....	40

## LIST OF FIGURES

1	Pilot-scale ESP and full-scale ESP-FF (TOXECON™) and ESP Hg removal efficiencies as a function of the ACI rate. ....	3
2	Pilot-scale ESP–FF and full-scale ESP-FF (TOXECON™) and ESP Hg removal efficiencies as a function of the ACI rate.....	4
3	Hg emissions for ACI combined with additives .....	6
4	Injection and sampling schematic of the PTC with an ESP .....	11
5	Flue gas compositions in Freedom lignite combustion.....	13
6	Mercury vapor concentration in Freedom coal flue gas – baseline.....	14
7	Mercury speciation across the ESP baseline data for Freedom coal, 300°F .....	15
8	Mercury vapor concentrations at the ESP inlet and outlet during DARCO® FGD carbon injection .....	16
9	Effect of NaCl and DARCO® FGD performance for mercury control in ESP .....	16
10	Ontario Hydro speciation across ESP with 18.4 lb/Macf DARCO® FGD injection.....	17
11	Mercury vapor concentrations at the ESP inlet and outlet during DARCO® FGD/NaCl injection .....	18
12	Mercury vapor concentrations at the ESP outlet during DARCO® FGD/NaCl injection long-term test.....	19
13	Mercury speciation across ESP with NaCl/DARCO® FGD carbon injection .....	20
14	Effect of SEA 2 and DARCO® FGD on mercury control in the ESP.....	20
15	Mercury vapor concentrations at the ESP inlet and outlet during EERC-treated FGD carbon injection .....	22
16	Mercury vapor concentration at the ESP outlet during HCl-treated FGD/NaCl injection .....	22
17	Mercury capture in the ESP with different sorbent injection.....	23

Continued . . .

## LIST OF FIGURES (continued)

18	Effects of other additives on mercury capture in an ESP .....	23
19	Mercury removal in an ESP with ALSTOM sorbent injection technologies.....	24
20	Injection and sampling schematic of the PTC with an ESP and <i>Advanced Hybrid™</i> filter. ....	27
21	Mercury speciation across the ESP and <i>Advanced Hybrid™</i> filter in Freedom coal flue gas .....	29
22	Mercury species across the <i>Advanced Hybrid™</i> filter with DARCO® FGD continuous injection, 300°F. ....	30
23	Mercury speciation across the retrofitted <i>Advanced Hybrid™</i> filter with 2.02 lb/Macf DARCO® FGD injection.....	31
24	Mercury removal in a retrofitted <i>Advanced Hybrid™</i> with DARCO® FGD injection .....	31
25	Mercury vapor species across the <i>Advanced Hybrid™</i> filter under DARCO® FGD.....	32
26	Mercury vapor species across the <i>Advanced Hybrid™</i> filter under DARCO® FGD.....	33
27	Effect of additives for mercury control in the <i>Advanced Hybrid™</i> filter .....	34
28	Effects of additives on mercury capture in a retrofitted <i>Advanced Hybrid™</i> filter .....	35
29	Mercury removal with FGD plus NaCl in the retrofitted <i>Advanced Hybrid™</i> filter .....	36
30	Mercury speciation across the retrofitted <i>Advanced Hybrid™</i> filter 2.57 lb/Macf DARCO® FGD plus 3.67 lb/Macf NaCl injection .....	36
31	The portable baghouse unit installed at Basin Electric’s Leland Olds Station for sorbent injection field tests.....	37
32	Mercury levels in the flue gas on Day 2, with increasing carbon injection rate to maintain a 2 lb/MMacf carbon injection rate in the baghouse while increasing the A/C ratio .....	39
33	Milestone chart.....	40

## LIST OF TABLES

1	Test Matrix for Unscrubbed Systems Equipped with ESPs – Task 1 .....	11
2	Coal Analysis of Freedom Lignite for Run PTC-FM-639 – Task 1 .....	12
3	ESP Hopper Ash Analysis Results – NaCl/FGD Injection – Task 1 .....	14
4	ESP Hopper Ash Analysis Results – SEA 2 Injection – Task 1 .....	21
5	Spray Dryer Test Sample Matrix (December 2003 run) – Task 2 .....	25
6	Test Matrix for Retrofitted <i>Advanced Hybrid</i> <sup>TM</sup> Filter – Task 4.....	28
7	ESP and <i>Advanced Hybrid</i> <sup>TM</sup> Filter Hopper Ash Analyses – Task 4.....	34
8	Portable Baghouse Slipstream (Days 1 and 2) Test Matrix at Leland Olds Unit 1 – Task 5 .....	38
9	Preliminary Data from Leland Olds Baghouse Sampling – Task 5 .....	39

# PILOT- AND FULL-SCALE DEMONSTRATION OF ADVANCED MERCURY CONTROL TECHNOLOGIES FOR LIGNITE-FIRED POWER PLANTS

## INTRODUCTION

North Dakota lignite-fired power plants have shown a limited ability to control mercury emissions in currently installed electrostatic precipitators (ESPs), dry scrubbers, and wet scrubbers (1). This low level of control can be attributed to the high proportions of  $\text{Hg}^0$  present in the flue gas. Speciation of Hg in flue gases analyzed as part of the U.S. Environmental Protection Agency (EPA) information collection request (ICR) for Hg data showed that  $\text{Hg}^0$  ranged from 56% to 96% and oxidized mercury ranged from 4% to 44%. The Hg emitted from power plants firing North Dakota lignites ranged from 45% to 91% of the total Hg, with the emitted Hg being greater than 85% elemental. The higher levels of oxidized mercury were only found in a fluidized-bed combustion system. Typically, the form of Hg in the pulverized and cyclone-fired units was dominated by  $\text{Hg}^0$  at greater than 85%, and the average amount of  $\text{Hg}^0$  emitted from North Dakota power plants was 6.7 lb/TBtu (1, 2).

The overall objective of this Energy & Environmental Research Center (EERC) project is to develop and evaluate advanced and innovative concepts for controlling Hg emissions from North Dakota lignite-fired power plants by 50%–90% at costs of one-half to three-fourths of current estimated costs. The specific objectives are focused on determining the feasibility of the following technologies: Hg oxidation for increased Hg capture in wet and dry scrubbers, incorporation of additives and technologies that enhance Hg sorbent effectiveness in ESPs and baghouses, the use of amended silicates in lignite-derived flue gases for Hg capture, and the use of Hg adsorbents within a baghouse. The scientific approach to solving the problems associated with controlling Hg emissions from lignite-fired power plants involves conducting testing of the following processes and technologies that have shown promise on a bench, pilot, or field scale: 1) activated carbon injection (ACI) upstream of an ESP combined with sorbent enhancement, 2) Hg oxidation and control using wet and dry scrubbers, 3) enhanced oxidation at a full-scale power plant using tire-derived fuel (TDF) and oxidizing catalysts, and 4) testing of Hg control technologies in the *Advanced Hybrid*<sup>TM</sup> filter insert.

## WORK PLAN

The work plan for this proposed project consists of six tasks outlined as follows:

- Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs
- Task 2 – Mercury Oxidation Upstream of Wet and Dry Scrubbers
- Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation
- Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the *Advanced Hybrid*<sup>TM</sup> Filter Technology



- Task 5 – Field Testing of Sorbents
- Task 6 – Project Reporting and Management

## BACKGROUND

North Dakota lignite-fired power plants have shown a limited ability to control Hg emissions in currently installed ESPs, dry scrubbers, and wet scrubbers (1). This low level of control can be attributed to the high proportions of  $\text{Hg}^0$  present in the flue gas. Speciation of Hg in flue gases analyzed as part of the EPA ICR for Hg data showed that  $\text{Hg}^0$  ranged from 56% to 96% and the oxidized mercury ranged from 4% to 44%. The Hg emitted from power plants firing North Dakota lignites ranged from 45% to 91% of the total Hg, with the emitted Hg being greater than 85% elemental. The higher levels of oxidized mercury were only found in a fluidized-bed combustion system. Typically, the form of Hg in the pulverized and cyclone-fired units was dominated by  $\text{Hg}^0$ , being greater than 85% elemental, and the average emitted from North Dakota power plants was 6.7 lb/Btu (1, 2).

The composition of a coal has a major impact on the quantity and form of Hg in the flue gas and, as a result, on the ability of air pollution control devices (APCDs) to remove Hg from flue gas. In general, North Dakota lignitic coals are unique because of a highly variable ash content, ash that is rich in alkali and alkaline-earth elements, high oxygen levels, high-moisture levels, and low chlorine content. Experimental results indicate that low-chlorine (<50 ppm) coal combustion flue gases (typical of North Dakota lignite) contain predominantly  $\text{Hg}^0$ , which is substantially more difficult to remove than  $\text{Hg}^{2+}$  (3). The generally high calcium contents of lignite coals may reduce the oxidizing effect of the already-low chlorine content by reactively scavenging chlorine species ( $\text{Cl}$ ,  $\text{HCl}$ , and  $\text{Cl}_2$ ) from the combustion flue gas. The level of chlorine in flue gases of recently tested North Dakota and Saskatchewan lignites ranged from 2.6 to 3.4 ppmv, respectively, while chlorine contents in the coal on a dry basis ranged from 11 to 18 ppmw, respectively.

### Mercury Control Options

The technologies utilized for the control of Hg will ultimately depend upon the EPA-mandated emission limits. Options being investigated have the potential to attain over 90% control of Hg emissions. The Hg control strategies at North Dakota lignite-fired power plants involve, first, the enhancement of existing control technologies and, second, investigation and development of new control technologies. The strategies include sorbent injection with and without enhancements upstream of an ESP or fabric filter (FF) and Hg oxidation upstream of a wet or dry flue gas desulfurization (FGD) system. The new technologies being investigated include Hg capture using the EERC's advanced hybrid particulate collector (AHPC) or the *Advanced Hybrid*<sup>TM</sup> filter gold-coated materials, baghouse inserts, and carbon beds (4).

Sorbent injection for removing Hg involves adsorption of Hg species by a solid sorbent injected upstream of a particulate control device such as an FF (baghouse) or ESP. Many

potential Hg sorbents have been evaluated (4). These evaluations have demonstrated that the chemical speciation of Hg controls its capture mechanism and ultimate environmental fate.

Activated carbon injection is the most mature technology available for Hg control. Activated carbons have the potential to effectively sorb  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  but depend upon the carbon characteristics and flue gas composition (4). Most activated carbon research has been performed in fixed-bed reactors that simulate relatively long-residence-time (gas–solid contact times of minutes or hours) Hg capture by an FF filter cake (5–7). However, it is important to investigate short-residence-time (seconds) in-flight capture of  $\text{Hg}^0$  because most of the coal-burning boilers in the United States employ cold-side ESPs for controlling particulate matter emissions. The projected annual cost for activated carbon adsorption of Hg in a duct injection system is significant. Carbon-to-mercury weight ratios of 3000:18,000 (lb carbon injected/lb Hg in flue gas) have been estimated to achieve 90% Hg removal from a coal combustion flue gas containing  $10 \mu\text{g}/\text{Nm}^3$  of Hg (1). More efficient carbon-based sorbents are required to enable lower carbon-to-mercury weight ratios to be used, thus reducing the costs. Recent testing conducted at the EERC, as shown in Figures 1 and 2, illustrates the effectiveness of sorbents injected upstream of the ESP and baghouse, respectively.

EERC pilot-scale ESP and ESP–FF Hg removal efficiencies for the Fort Union lignite coals from Saskatchewan and North Dakota (Poplar River and Freedom coals) flue gases are compared in Figures 1 and 2 to those obtained at full-scale utility boilers where activated carbons were injected into a bituminous coal combustion flue gas upstream of a compact hybrid particulate collector (TOXECON™) (pulse-jet FF) and into bituminous and Powder River Basin

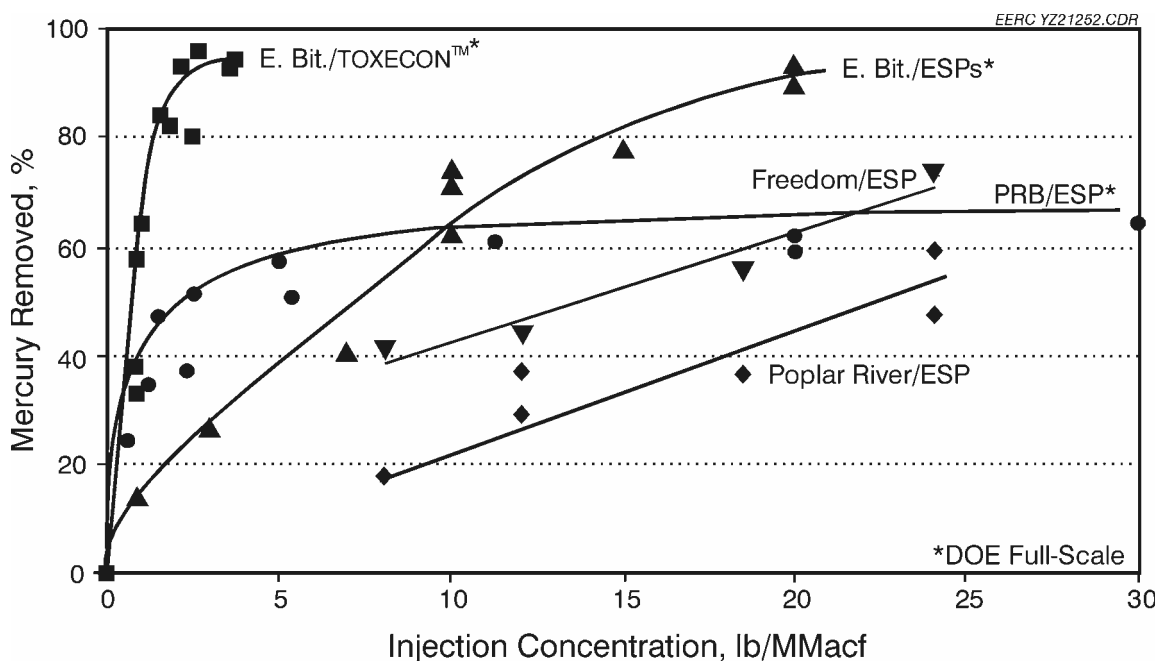


Figure 1. Pilot-scale ESP (1) and full-scale ESP-FF (TOXECON™) and ESP (9) Hg removal efficiencies as a function of the ACI rate.

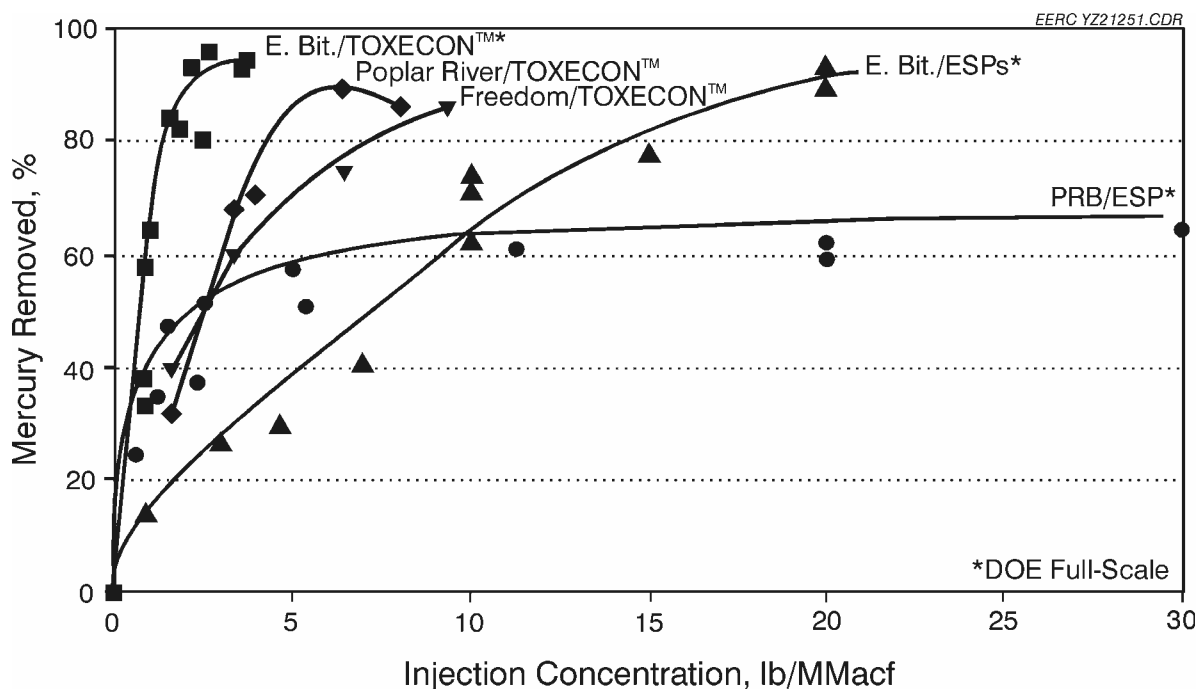


Figure 2. Pilot-scale ESP-FF (1) and full-scale ESP-FF (TOXECON™) and ESP (9) Hg removal efficiencies as a function of the ACI rate.

(PRB) subbituminous coal combustion flue gases upstream of an ESP. Coal type (i.e., composition) is an important parameter that affects the Hg removal efficiency of a control device. During the pilot-scale lignite and utility-scale eastern bituminous coal tests, Hg removal efficiency increased with increasing ACI rates. Conversely, Hg removal efficiency was never greater than 70%, regardless of the ACI rate into the PRB subbituminous coal combustion flue gas. This limitation is probably caused by the low amount of acidic flue gas constituents, such as HCl, that promote Hg-activated carbon reactivity.

Testing conducted at lignite-fired power plants equipped with a spray dryer baghouse firing Fort Union lignite indicated poor performance of conventional ACI to control Hg (10). The results indicate control efficiency of less than 35% for DARCO® FGD and lignite-activated carbon (LAC). The poor results are due to the low-acid-gas-containing flue gas and the high proportion of  $Hg^0$  in the flue gas stream. The iodine-impregnated activated carbon (IAC) showed approximately 90% control.

Researchers at the EERC and elsewhere are striving to attain a better understanding of Hg species reactions on activated carbon surfaces in order to produce more efficient sorbents. Functional groups containing inorganic elements such as chlorine or sulfur appear to have a significant role in bonding Hg (11–13). Recently, detailed analysis of sorbents derived from lignites exposed to flue gas and  $Hg^0$  indicated the key species impacting oxidation and retention of Hg on the surface of the carbon contain chlorine and sulfur (14, 15). The chlorine reacts to form organically associated chlorine on the surface, and it appears that the organically associated chlorine on the carbon is the key site responsible for bonding with the  $Hg^{2+}$  species.

Amended silicate injection shows promise in controlling Hg emissions at coal-fired power plants (16). The amended silicates have shown improvement factors of 1.5–2 in controlling Hg emissions over activated carbon from subbituminous coal testing in a pilot-scale test. The amended silicates have not been tested using North Dakota lignites.

### Mercury Oxidation

Mercury oxidation technologies being investigated for Fort Union lignites include catalysts, chemical agents, and cofiring materials. The catalysts that have been tested include a selective catalytic reduction (SCR) catalyst for NO<sub>x</sub> reduction, noble metal-impregnated catalysts, and oxide-impregnated catalysts. The chemical agents include chlorine-containing salts and cofiring fuels that contain oxidizing agents (10).

SCR catalysts were tested for their ability to oxidize Hg; results were mixed. Mercury speciation sampling conducted upstream and downstream of SCR catalysts at power plants that fire bituminous and subbituminous coals (17) showed evidence of mercury oxidation across SCR catalysts when bituminous coals are fired. However, when subbituminous coals are fired, the results indicate limited oxidation. More testing needs to be conducted on low-rank coals. The ability of the SCR system to contribute to oxidation appears to be coal-specific and is related to the chloride, sulfur, and calcium content of the coal, as well as temperature and specific operation of the SCR catalyst including space velocity.

Mercury oxidation catalysts have shown high potential to oxidize Hg<sup>0</sup>. Results in testing a slipstream at a North Dakota power plant indicated over 80% conversion to oxidized mercury for periods of up to 6 months (10). Tests were also conducted using iron oxides and chromium, with little success of oxidation. Zygarlicke and others (18) have conducted short-term pilot-scale testing with maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) additions and were able to transform about 30% of the Hg<sup>0</sup> in North Dakota lignite combustion flue gases to Hg<sup>2+</sup> and/or Hg(p) and, with an injection of a small amount of HCl (100 ppmv), nearly all of the Hg<sup>0</sup> to Hg<sup>2+</sup>. Theoretically, the use of chloride compounds to oxidize Hg<sup>0</sup> to Hg<sup>2+</sup> makes sense. The evidence includes chemical kinetic modeling of bench-scale test results, indicating that the introduction of chloride compounds into the high-temperature furnace region will most likely result in the production of atomic chlorine and/or molecular chlorine, which are generally thought to be the dominant Hg<sup>0</sup> reactants in coal combustion flue gases (4).

Fuel additives for mercury oxidation and sorbent enhancement have recently been tested at the EERC. The results of the addition of materials with coal at very low levels along with the ACI upstream of an ESP–FF, *Advanced Hybrid*<sup>TM</sup>, and ESP-only are illustrated in Figure 3. The first part of the figure shows the baseline data for Hg emissions ranging from 9 to 12 μg/Nm<sup>3</sup>, with 80%–90% of the Hg in the elemental form. The second case is ACI followed by the addition of Additive 2, showing a reduction in Hg emissions to 90% removal. The third case is the *Advanced Hybrid*<sup>TM</sup> filter, which produced nearly 90% control efficiency. The final ESP-only case also indicated up to 90% control. The control efficiency for the ESP-only case showed significant potential improvement over past results obtained with the ESP-only illustrated in Figure 1. This technology also has the potential to improve dry FGD baghouse control efficiency.

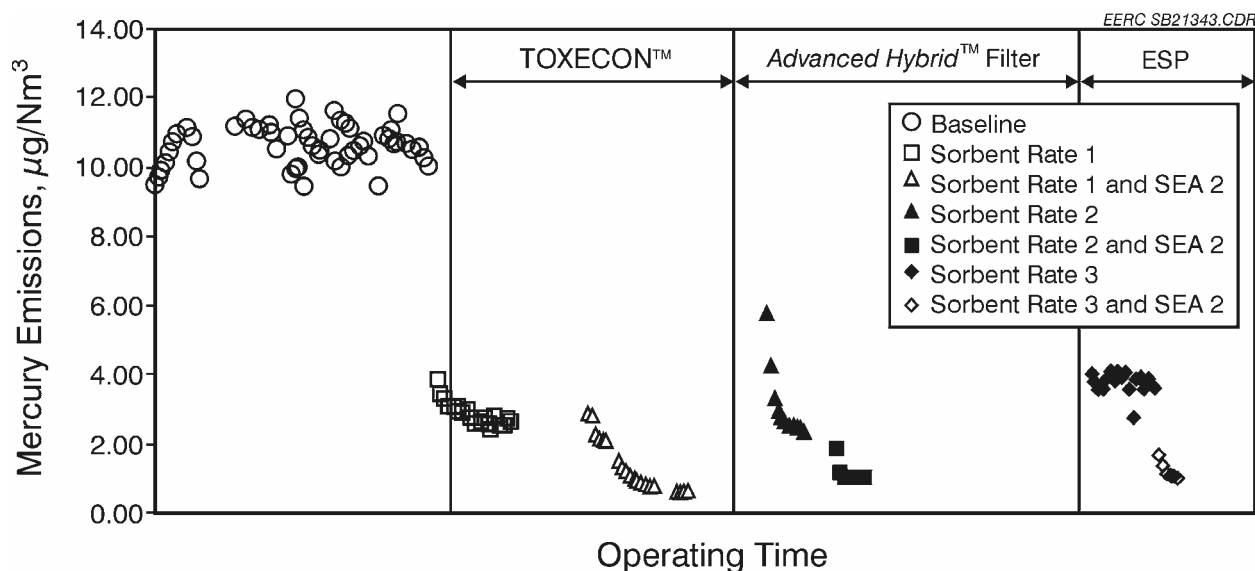


Figure 3. Hg emissions for ACI combined with additives.

Sorbent enhancement technologies (also referred to as additives [SEAs]) have also been investigated by ALSTOM Power, Inc. The sorbent preparation system enhances sorbent performance by changing the physical and chemical nature of the sorbent. The enhancement is expected to be applicable to a significant number of sorbents currently utilized for Hg control. The potential for sorbent enhancement has shown an increase from 68% to over 90% capture of Hg. These tests evaluated the performance of baseline and enhanced sorbents in entrained flow. Sorbents were injected in a duct with synthetic flue gas followed by an ESP.

Cofiring TDF at Otter Tail Power Company's Big Stone Plant has been suspected to contribute to very high reactivity of Hg with fly ash and also with carbon sorbents while a low-chlorine PRB coal is fired (19). During periods of operation that coincide with TDF being cofired, enhanced Hg oxidation and removal of Hg by a particulate control device (PCD) have been observed. When about 3%–5% (Btu basis) TDF was cofired with coal at the power plant, measurements showed that the average PCD inlet Hg speciation was 55% particulate bound, 38% oxidized, and 6.4% elemental. Without carbon injection to the PCD, the natural Hg capture efficiency of the PCD was 49%. Furthermore, a carbon injection rate of 24 kg carbon/million m<sup>3</sup> flue gas resulted in a 91% total Hg capture efficiency at the PCD. These field test results indicate that cofiring TDF has the effect of changing the speciation of Hg at the inlet to the PCD, which facilitates Hg collection at the PCD.

Since 1995, DOE has supported development of a new concept in particulate control called the AHPC (19). The AHPC has been licensed to W.L. Gore & Associates, Inc., and is now marketed as the *Advanced Hybrid™* filter by Gore. The *Advanced Hybrid™* combines the best features of ESPs and baghouses in a unique configuration, providing major synergism between the two collection methods, both in the particulate collection step and in the transfer of dust to the hopper. The *Advanced Hybrid™* filter provides ultrahigh collection efficiency, overcoming the problem of excessive fine-particle emissions with conventional ESPs, and it solves the

problem of reentrainment and re-collection of dust in conventional baghouses. The *Advanced Hybrid™* filter appears to have unique advantages for Hg control over baghouses or ESPs as an excellent gas–solid contactor. The *Advanced Hybrid™* filter technology can be a very cost-effective retrofit technology for plants with existing ESPs.

## **EXPERIMENTAL**

### **Objective and Goals**

The goal of this work is to develop advanced, innovative mercury control technologies to reduce mercury emissions by 50%–90% in flue gases typically found in North Dakota lignite-fired power plants at costs of one-half to three-fourths of current estimated costs. Power plants firing North Dakota lignite produce flue gases that contain >85% elemental mercury, which is difficult to collect. The specific objectives are focused on determining the feasibility of the following technologies: mercury oxidation for increased mercury capture in dry scrubbers and the use of mercury adsorbents within a baghouse.

## **PLANNED SCOPE OF WORK**

### **Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs**

This task will evaluate and further the ability to control Hg emissions in lignite-fired power systems equipped with an ESP, as well as provide valuable information for enhancing Hg control in other unscrubbed systems. Testing will be performed using sorbent injection on the EERC's particulate test combustor (PTC) equipped with an ESP to evaluate Hg sorbent effectiveness in coal combustion flue gases.

This task will include testing for a full week with up to two North Dakota lignite coals with one activated carbon and ADA Technologies, Inc.'s, Amended Silicate™. In addition, a sorbent enhancement technology developed by ALSTOM Power, Inc., will be used to enhance a sorbent for injection in the flue gas duct upstream of the ESP. During ACI, several additives and sorbent enhancements will be tested to quantify the improvements in Hg removal with each. The initial testing will involve shorter-term screening tests for evaluation of the sorbent enhancement additives (roughly two a day). A final full-day test will be performed to obtain longer-term results on the performance of a selected additive. This final additive will be selected based on performance during screening tests and with consideration of cost, availability, and any issues associated with use in a utility system. Based on the test results, initial economic evaluations will be performed to determine the cost savings per pound of Hg removal in comparison to the baseline case of ACI without additives.

## **Task 2 – Mercury Oxidation Upstream of Wet and Dry Scrubbers**

### ***Task 2.1 – Elemental Mercury Oxidation Additives***

Potential  $\text{Hg}^0$  oxidation additives will be evaluated using the PTC equipped with the refurbished spray dryer absorber (SDA) and AHPC. Pilot-scale testing will involve a North Dakota lignite coal with short-term (1- to 2-h) screening tests of several oxidation additives including chloride compounds (e.g., sodium chloride, hydrogen chloride, calcium chloride) and potassium iodide, followed by longer-term (8- to 10-h) evaluations of two or more of the most promising additives. In most cases, the additives will be blended with the coals. Gaseous HCl will be injected into the PTC.

$\text{Hg}^0$  and total Hg levels will be measured on a nearly continuous basis using a continuous mercury monitor (CMM) at the inlet and outlet locations of the SDA. Slaked lime slurry feed and the SDA product solids will be analyzed for Hg content. Additive blend ratios and injection rates will be varied to evaluate the effectiveness of additives to oxidize  $\text{Hg}^0$ . Economic analyses will be performed for the additives that are most effective.

### ***Task 2.2 – Sorbent Injection***

NORIT Americas Inc., DARCO<sup>®</sup> FGD, and lignite-based activated (steam activated at 800°C, 1472°F) Luscar char (derived from Fort Union lignite) will also be injected upstream of the SDA while a North Dakota lignite is burned in the PTC. One of the sorbents will be pretreated with an EERC proprietary material to enhance its sorption capacity. FGD, activated Luscar char, and the pretreated sorbent will be injected in the absence and presence of the most effective  $\text{Hg}^0$  oxidation additive identified in Task 2.2. In addition, a proprietary sorbent enhancement technology developed by ALSTOM will be tested. CMMs will be used to measure  $\text{Hg}^0$  and total Hg at the inlet and outlet of the SDA during each test. After each test, slaked lime slurry feed and the SDA product solids will be analyzed for Hg and carbon contents.

## **Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation**

### ***Task 3.1 – Impacts of Cofiring on Tire-Derived Fuels***

The efforts in this subtask involve testing the ability of cofiring TDF with North Dakota lignite to increase the oxidized and particulate forms of mercury at a fluid bed-fired power plant (Montana–Dakota Utilities Heskett Station Unit 2, 85 MW, ESP). Testing will include a baseline run firing 100% lignite at full load and up to 10% TDF (Btu basis). Hg and Cl species levels in the flue gas phase will be measured at the inlet and the outlet of the ESP with and without cofiring the TDF. Coal and TDF will be analyzed for basic proximate, ultimate, sulfur, and ash compositional analysis and Cl, Zn, and Hg. Total Hg collection efficiency of the ESP and the Hg speciation information will be determined.

### ***Task 3.2 – Impacts of Oxidation Catalysts – Coyote Station Slipstream Testing***

This task involves testing a Hg oxidation agent. Maghemite combined with very small amounts of HCl has been shown to oxidize  $\text{Hg}^0$  in simulated flue gases. Currently, a slipstream reactor to test  $\text{NO}_x$  reduction catalysts is being installed at Otter Tail Power Company's Coyote Station in North Dakota under an existing EERC project. In Task 3.2, maghemite will be incorporated into a catalyst matrix by Haldor Topsoe, Inc., and placed into the reactor. Small amounts of HCl will be added, and the impact on Hg speciation will be measured across the reactor.

### **Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the *Advanced Hybrid*<sup>TM</sup> Filter Technology**

This task includes reconfiguring the PTC with an ESP followed by the *Advanced Hybrid*<sup>TM</sup> filter system to simulate a full-scale retrofit system. The single-wire tubular ESP will be operated at slightly reduced power to simulate the first one or two ESP fields in a full-scale system, with a goal of removing approximately 90% of the fly ash. Flue gas exiting the ESP with a reduced fly ash level will be routed to the pilot-scale (200-acfm) *Advanced Hybrid*<sup>TM</sup> filter unit.

Two sorbents (activated carbon and silicate-based sorbent) will be injected near the *Advanced Hybrid*<sup>TM</sup> filter inlet. Both continuous and batch injection modes will be tested at a flue gas temperature of 300°F. Specific sorbent injection rates will be determined based on the measured Hg concentration in the flue gas. For continuous injection, the feed rate will be varied from 2500 to 12,000 lb sorbent/lb Hg, and for batch injection the ratio will be set at 6000:1. The sorbent that shows the best performance will be tested at a higher flue gas temperature of 400°F, both in continuous and batch injection modes. CMMs will be used to measure  $\text{Hg}^0$  and total Hg vapor at the ESP inlet, the *Advanced Hybrid*<sup>TM</sup> filter inlet, and the *Advanced Hybrid*<sup>TM</sup> filter outlet. Mercury sampling with the Ontario Hydro (OH) method will be conducted to provide Hg species information, dust loading, and particulate collection efficiencies for the retrofit *Advanced Hybrid*<sup>TM</sup> filter unit. EPA Method 26A sampling will be carried out at the *Advanced Hybrid*<sup>TM</sup> filter inlet to determine the chloride level in flue gas entering into the *Advanced Hybrid*<sup>TM</sup> filter unit. Results from the tests will be reduced, compiled, interpreted, and reported. Mercury removal efficiencies for both sorbents will be calculated, compared, and reported across the ESP, the *Advanced Hybrid*<sup>TM</sup> filter, and the ESP–*Advanced Hybrid*<sup>TM</sup> filter.

### **Task 5 – Field Testing of Sorbents (revised January 2004)**

This task will test how effectively Hg can be captured by using a sorbent-based technology in conjunction with a pulse-jet baghouse (PJBH) at a power plant in North Dakota. This task's work plan formerly included evaluation of a Gore technology consisting of a proprietary baghouse insert downstream of the FF that has shown a high potential to control Hg. However, Gore's recent decision to abandon its mercury research program has resulted in elimination of the Gore technology inclusion in the planned scope of work. Additional sorbent evaluations will fill the void. An existing baghouse will be skid-mounted and transported to a power plant in North Dakota and connected in slipstream fashion to allow for testing actual flue gases. Additions to the existing baghouse unit for remote field application will include a control room



for remote operation, piping and flanges for connection to plant ductwork, a variable-speed fan, and a sorbent injection system for Hg control. The PJBH can operate for much longer periods of time than can the pilot-scale AHPC.

The skid-mounted baghouse will be installed downstream of an existing PCD such as an ESP. CMMs will be used to measure Hg<sup>0</sup> and total Hg vapor at various monitoring ports in the system. Mercury sampling with the OH method will be conducted to provide Hg species information, dust loading, and particulate collection efficiencies. In certain cases, EPA Method 101A may be used to determine the total Hg (only) removed across the baghouse system.

## RESULTS AND DISCUSSION

### **Task 1 – Mercury Control Enhancement for Unscrubbed Systems Equipped with ESPs**

#### ***Pilot-Scale Facility and Test Plan***

The pilot-scale test was started on September 8, 2003, and was completed on September 19, 2003. A 550,000-Btu/hr pulverized coal (pc)-fired unit, known as the PTC, was used to fire lignites and test mercury control options. The coal combustion flue gas exiting the PTC was cooled down to a nominal temperature of 149°C (300°F) and then was introduced into a single-wire tubular ESP unit. Figure 4 shows the schematic diagram of the system. Furnace additives were added to coal prior to introduction to the furnace. Mercury sorbents were fed with a K-Tron dual-screw feeder upstream of the ESP. The feeder was calibrated prior to the start of carbon injection. In addition, the weight of carbon added during a run was divided by the time of injection to provide an average feed rate. According to the calibration data and weight-of-added-carbon data, the feeder appeared to provide a very steady and consistent feed rate within a few percentages of the target rate. The carbon feed and injection system worked very well, and there were no problems with inconsistent feeding or plugging of the feeder or injection system.

CMMs were used to monitor mercury vapor concentrations at the ESP inlet (Site 1) and outlet (Site 2) 24 h per day for the entire testing period. Several OH method samples (ASTM D6784 Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources) were collected at the ESP inlet and outlet throughout the testing period as verification of the CMM data.

Fourteen tests were completed to evaluate various sorbent and mercury oxidant performance on mercury removal across the ESP as functions of feed rate. A detailed test matrix is listed in Table 1. Ten additional tests were performed to evaluate mercury control with the *Advanced Hybrid*<sup>TM</sup> filter and are summarized under Task 4 of this Results and Discussion section.

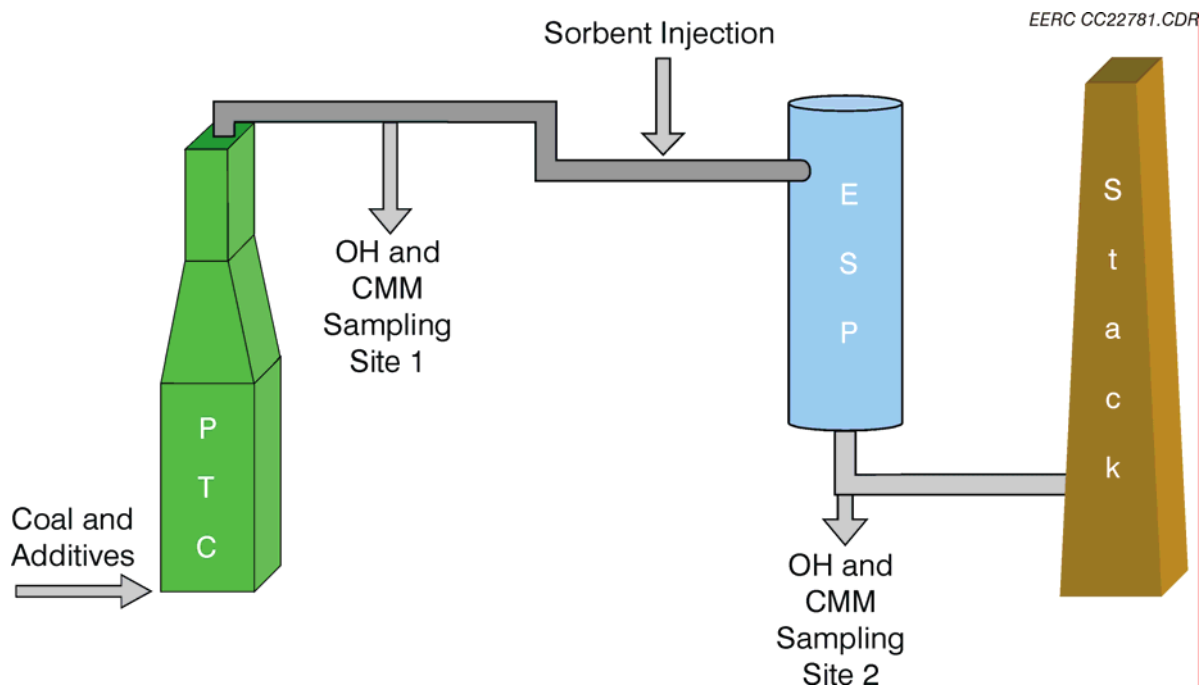


Figure 4. Injection and sampling schematic of the PTC with an ESP.

**Table 1. Test Matrix for Unscrubbed Systems Equipped with ESPs – Task 1**

Test No.	Mercury Oxidant Additive		Sorbent	
	Category	Injection Rate, lb/Macf	Category	Injection Rate, lb/Macf
T1-1(Baseline)	None	NA	None	NA
T1-2	None	NA	DARCO <sup>®</sup> FGD	2.75–18.4
T1-3	NaCl	3.76–14.7	None	NA
T1-4	NaCl	3.76–14.7	DARCO <sup>®</sup> FGD	2.75–4.59
T1-5	SEA 2	1.84–7.34	None	NA
T1-6	SEA 2	1.84	DARCO <sup>®</sup> FGD	2.57
T1-7	NaCl	7.34–11.0	HCl-treated FGD	2.57–4.59
T1-8	None	NA	EERC-treated carbon	1.84–2.75
T1-9	SEA 2	1.84	EERC-treated carbon	2.75
T1-10	Zn	7.34	None	NA
T1-11	Zn and NaCl	7.34–11.0	None	NA
T1-12	None	NA	Na <sub>2</sub> S <sub>4</sub> (solution)	0.89–6.67
T1-13	CaCl <sub>2</sub>	11	DARCO <sup>®</sup> FGD	0–4.59
T1-14	None	NA	ALSTOM sorbent	1.1–3.1

### *Coal and Combustion Flue Gas Analyses*

North Dakota Freedom lignite was tested in the PTC at the EERC. The proximate and ultimate analysis data for the Freedom lignite are reported in Table 2, showing a concentration of mercury in the range of 0.0503–0.0515  $\mu\text{g/g}$  (dry basis), with a mean value of 0.0508  $\mu\text{g/g}$ .

**Table 2. Coal Analysis of Freedom Lignite for Run PTC-FM-639 – Task 1**

Proximate Analysis, wt%	As Sampled	Moisture Free
Moisture Content	31.90	NA
Volatile Matter	30.70	45.05
Fixed Carbon	29.12	42.79
Ash	8.29	12.16
Ultimate Analysis, wt%		
Hydrogen	6.33	4.10
Carbon	41.26	60.55
Nitrogen	0.78	1.15
Sulfur	0.73	1.07
Oxygen	42.61	20.97
Ash	8.29	12.16
Mercury Concentration in Coal, $\mu\text{g/g}$		
Sample 1		0.0503
Sample 2		0.0507
Sample 3		0.0515
Sample 4		0.0505
Mean		0.0508

Based on the proximate and ultimate analysis data, it was calculated that 1 lb of coal would produce 89 scf of dry flue gas normalized to a 3.0% oxygen level. From the mercury content in raw coal, the total mercury concentration in flue gas was expected to be 7.2  $\mu\text{g/m}^3$  of dry flue gas (at a 3% oxygen level).

The flue gas compositions,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}_x$ , and  $\text{SO}_2$ , at the combustor outlet were monitored during the entire testing period, and hourly average values were calculated and plotted as a function of operating time as shown in Figure 5. The  $\text{CO}$  concentration was in the range 3–6 ppm for most of the testing period, indicating complete coal combustion.  $\text{CO}$  spikes were observed on September 10–12, 2003, showing somewhat incomplete coal combustion at that time. The  $\text{SO}_2$  concentration in the flue gas ranged from 300 to 1200 ppm, depending on the coal feed rate, while the theoretical value of the  $\text{SO}_2$  concentration was calculated at 1026 ppm, based on sulfur content and proximate and ultimate coal analyses. The  $\text{NO}_x$  concentration in the flue gas was 221–770 ppm. The  $\text{HCl}$  concentration in flue gas was also measured using EPA Method 26, showing 0.58–1.45 ppm. Because of the low levels of  $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{SO}_2$ , and  $\text{HCl}$  and historical data, most mercury in the Freedom lignite flue gas was expected to be in the elemental vapor phase ( $\text{Hg}^0$ ).

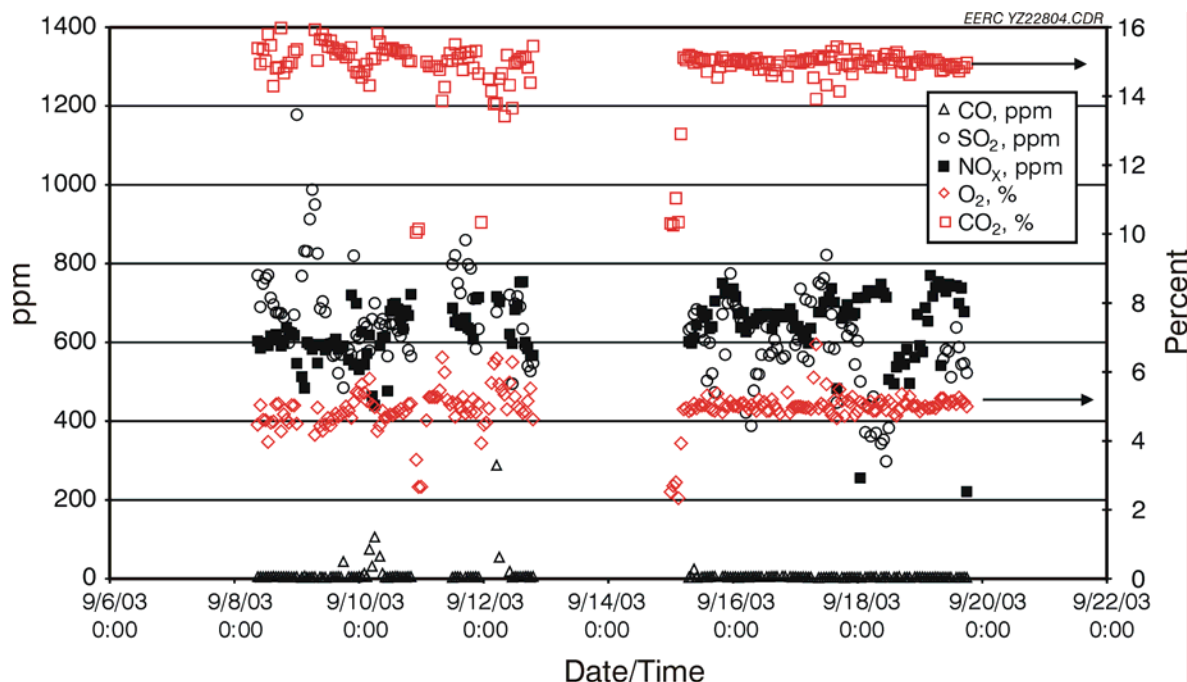


Figure 5. Flue gas compositions in Freedom lignite combustion.

### ***Mercury Speciation Across the ESP in the Baseline Test***

*Test T1-1 (Baseline).* During the pilot-scale test, Freedom lignite with a mean mercury content of 0.05  $\mu\text{g/g}$  (dry basis) was combusted at a nominal feed rate of 87 lb/hr. The coal combustion flue gas exiting the PTC was cooled down to a nominal temperature of 149°C (300°F) and then was introduced into a single-wire tubular ESP unit. The ESP was operated at 40–60 kV with a corona current of 4.0 mA. The collection plates and electrodes were rapped every 120 min. The hopper ash was emptied between tests. Two CMMs were used to monitor mercury vapor concentrations at the ESP inlet and outlet. OH method samples were collected to verify the CMM data. The purpose of the baseline test (T1-1) was to establish speciated mercury concentrations in Freedom lignite flue gas and determine whether there was a change in speciation across the ESP unit. Based on CMM data, the daily average mercury vapor concentrations in Freedom lignite combustion flue gas, both total and speciated, are shown in Figure 6. The error bars represent plus or minus one standard deviation. No particulate mercury for the CMM is shown because the flue gas was sampled through a filter. Oxidized mercury vapor in the flue gas was in the range of 0.09–1.30  $\mu\text{g}/\text{Nm}^3$ , while elemental mercury ( $\text{Hg}^0$ ) vapor was dominant, in the range of 5.52–8.13  $\mu\text{g}/\text{Nm}^3$ . The total mercury vapor concentration ( $\text{Hg}_{\text{gas}}$ ) in the flue gas varied from 6.8 to 9.2  $\mu\text{g}/\text{Nm}^3$  (dry flue gas, 3% O<sub>2</sub>), showing an average mercury level of 7.57  $\mu\text{g}/\text{Nm}^3$ , compared to the theoretical value of 7.2  $\mu\text{g}/\text{Nm}^3$  obtained from the coal combustion calculation based on the coal analysis. The above CMM data indicate that most of the mercury released from Freedom lignite combustion was in vapor phase before it entered into the ESP and elemental mercury vapor was the dominant species.

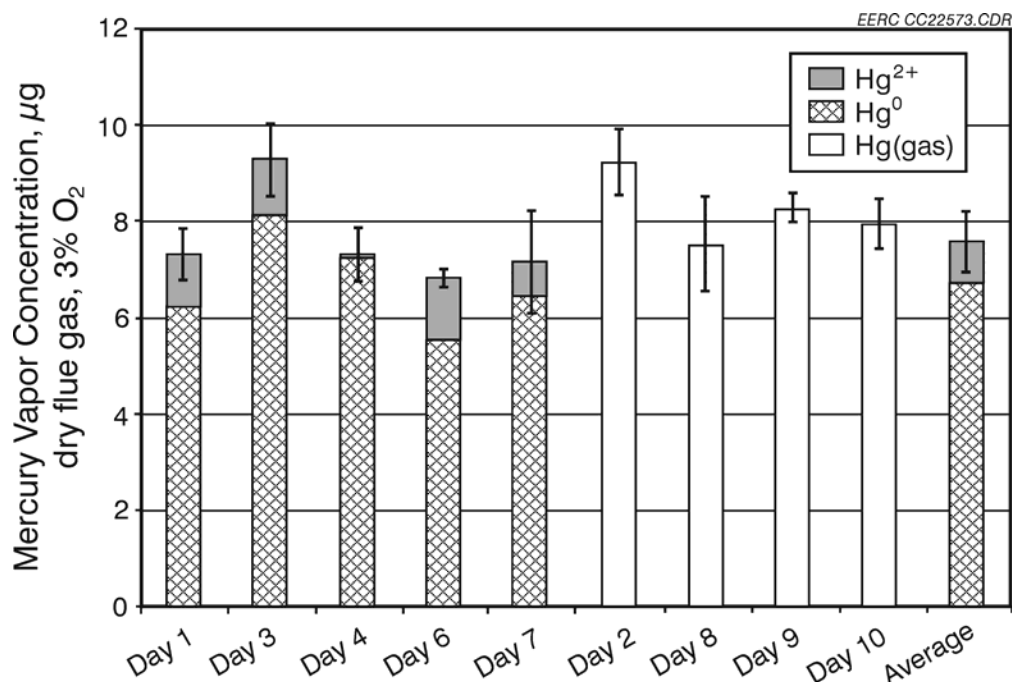


Figure 6. Mercury vapor concentration in Freedom coal flue gas – baseline.

To determine inherent mercury capture by fly ash across the ESP, mercury concentrations were measured with CMMs and the OH method both at the ESP inlet and outlet, and the results are plotted in Figure 7. Both methods indicate that the majority of mercury was present as elemental mercury vapor, with a small fraction (10.9%–12.9%) of oxidized mercury and nearly no particulate associated mercury at the ESP inlet. The total mercury concentration at the ESP outlet was almost the same as the ESP inlet, showing virtually no mercury capture across the ESP due to the low level of particulate mercury in the flue gas, which is very typical for North Dakota lignite with the ESP configuration. Comparison between the two sampling methods shows consistent results, with the OH method measurement slightly higher than the CMM results. ESP hopper ash was collected to analyze mercury content, loss on ignition (LOI), and chlorine and sodium concentrations. The results are listed in Table 3. The mercury content in the ESP hopper ash was 0.0139 μg/g, close to the 0.003–0.00783 μg/g at the ESP inlet, as indicated by the OH method data. This was not surprising based on the low levels of LOI (0.35%) and chlorine (206 μg/g) in the ESP hopper ash.

**Table 3. ESP Hopper Ash Analysis Results – NaCl/FGD Injection – Task 1**

	Baseline	DARCO <sup>®</sup> FGD	NaCl	NaCl + DARCO <sup>®</sup> FGD
LOI, %	0.35	1.28	0.46	0.94
Mercury, μg/g	0.0139	0.189	0.198	0.381
Chlorine, μg/g	206	NA	3820	5440
Sodium, μg/g	11,200	NA	12,200	18,700

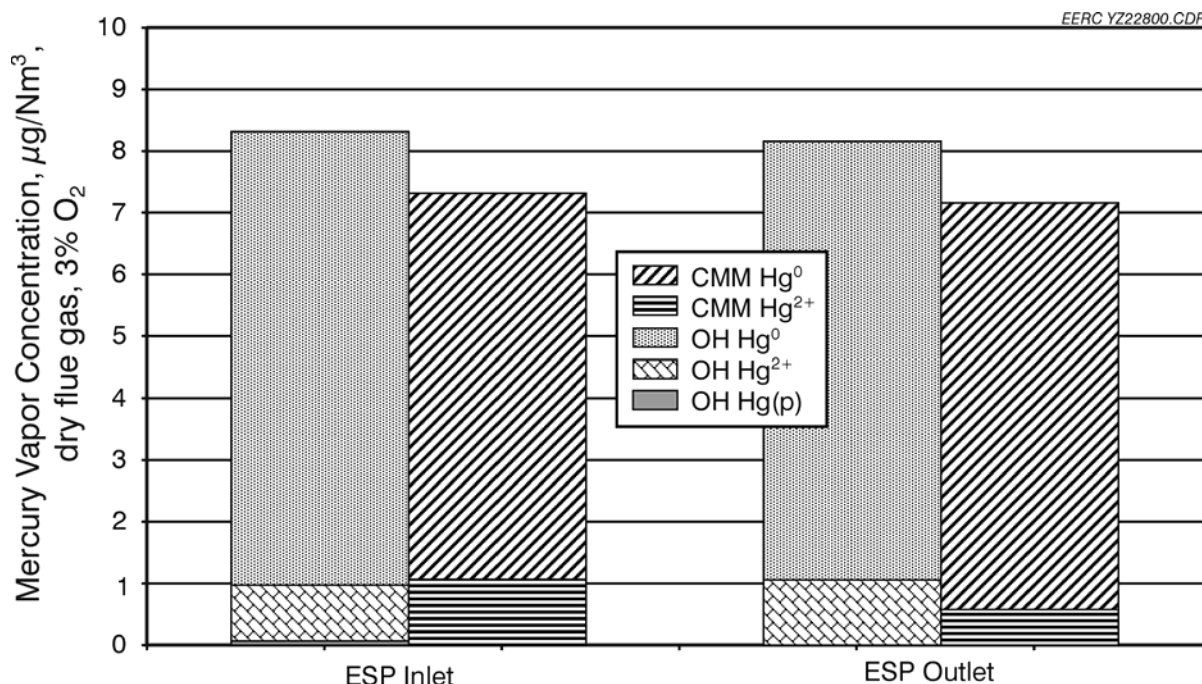


Figure 7. Mercury speciation across the ESP baseline data for Freedom coal, 300°F.

### ***Mercury Control Technology Results***

Mercury removal across the ESP was evaluated with sorbent injection, mercury oxidant addition, and a combination of sorbent and mercury oxidant. The sorbents were injected upstream of the ESP, while the mercury oxidants were added to the coal prior to introduction to the furnace. As listed in Table 1, the sorbents included DARCO<sup>®</sup> FGD activated carbon, EERC pretreated activated carbon, and ALSTOM sorbent technology. Mercury oxidants included NaCl,  $\text{CaCl}_2$ , Zn, and SEA 2.

*Tests T1-2 to T1-4.* Two tests were performed to evaluate DARCO<sup>®</sup> FGD carbon, mercury oxidant NaCl, and their combination on mercury removal in Freedom flue gas across the ESP. DARCO<sup>®</sup> FGD carbon was injected upstream of the ESP at varied feed rates from 4.59 to 18.4 lb/Macf. Figure 8 shows the temporal variation in total mercury vapor concentration (measured by CMM) downstream from the ESP while the total mercury vapor concentration at the ESP inlet was in a relatively stable range of 8–10  $\mu\text{g}/\text{Nm}^3$ . Mercury removal efficiencies across the ESP were calculated based on the CMM data at the ESP inlet and outlet and are plotted as a function of injection rate in Figure 9. The mercury removal was 51.5% at 4.59 lb/Macf, increased to 59% at 9.18 lb/Macf, and reached 67.2% at 18.4 lb/Macf sorbent injection. The OH mercury speciation data were collected at the 18.4 lb/Macf injection test (Figure 10), showing DARCO<sup>®</sup> FGD carbon only captured 60% of the total mercury in flue gas. Since there are low levels of particulate associated mercury in flue gas, the total mercury collection efficiency calculated based on the OH data is similar to the CMM results (also shown in Figure 9). During DARCO<sup>®</sup> FGD carbon injection, the LOI level in the ESP hopper ash increased to

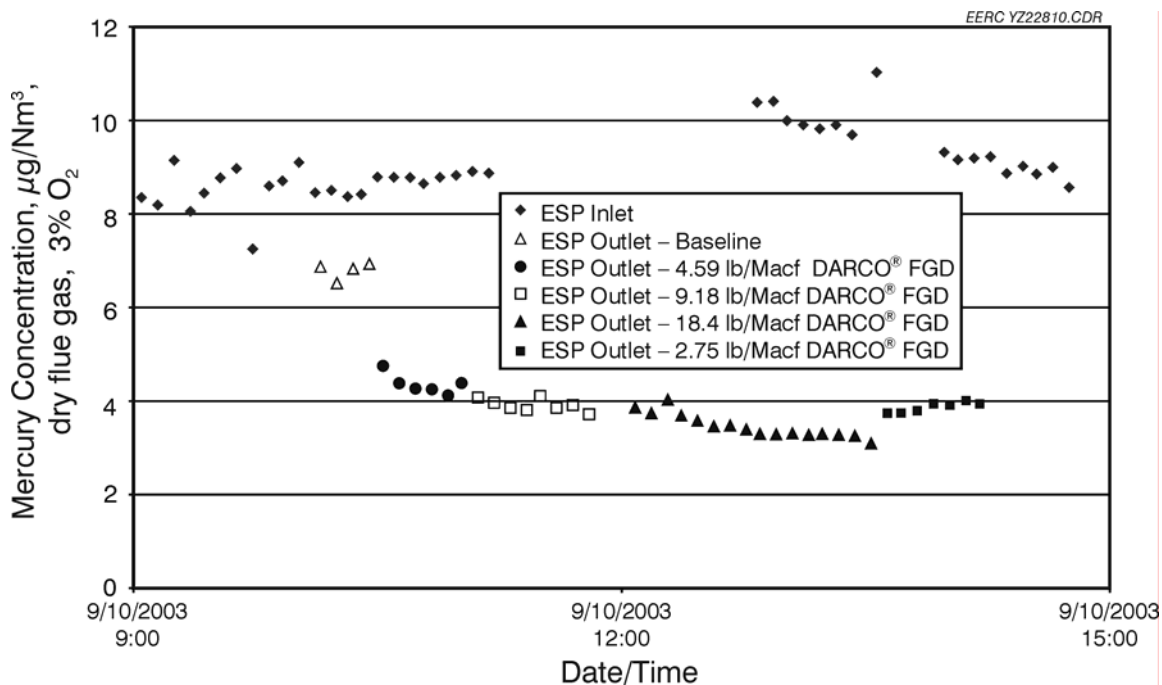


Figure 8. Mercury vapor concentrations at the ESP inlet and outlet during DARCO® FGD carbon injection (Freedom coal, 300°F).

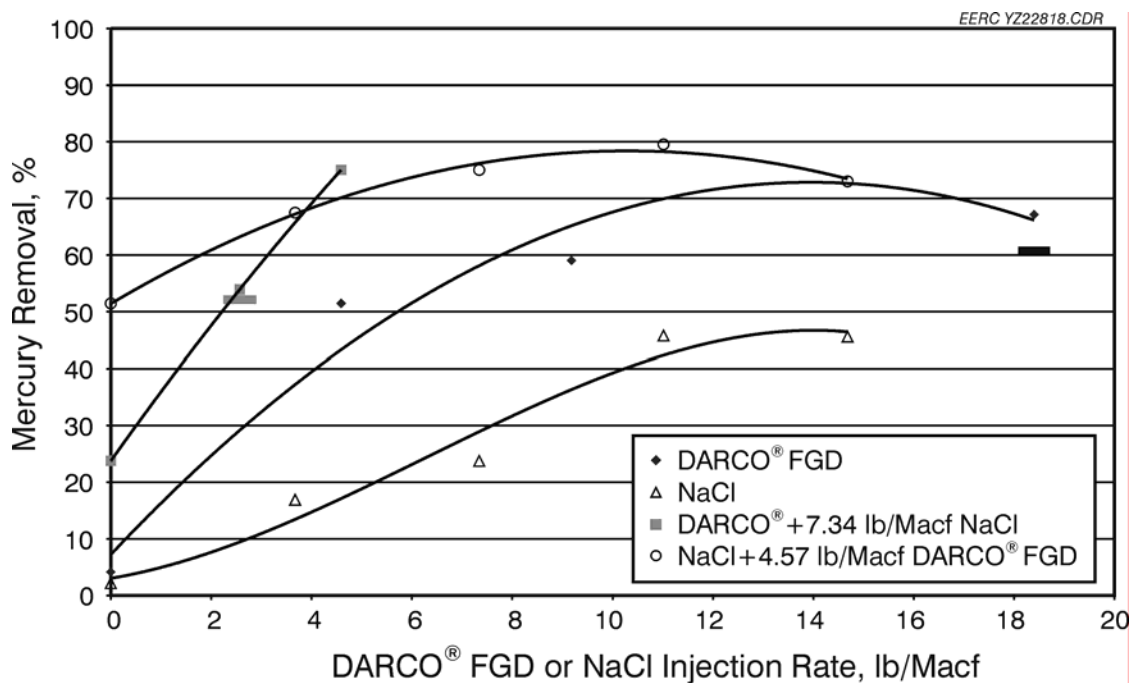


Figure 9. Effect of NaCl and DARCO® FGD performance for mercury control in ESP.

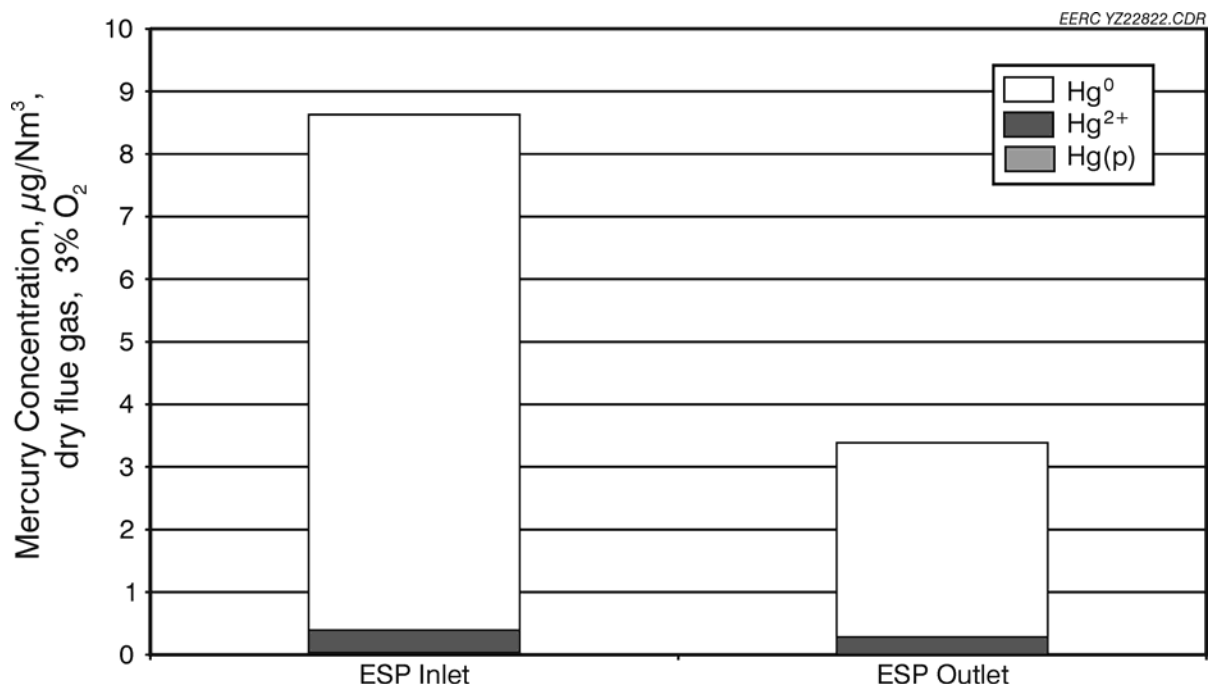


Figure 10. Ontario Hydro speciation across ESP with 18.4 lb/Macf DARCO<sup>®</sup> FGD injection (Freedom, 300°F).

1.28% and the mercury concentration was 0.189 µg/g, higher than the 0.0139 µg/g in baseline test (also listed in Table 3).

The above results indicate that large amounts of DARCO<sup>®</sup> FGD carbon are required for efficient mercury removal across the ESP for Freedom lignite flue gas due to the low reactivity and the mass transfer limit between gaseous mercury and the in-flight DARCO<sup>®</sup> FGD carbon.

Previous research at the EERC indicated that cofiring NaCl and coal can enhance mercury reactivity with sorbents and mercury oxidation in flue gas. Herein, solid NaCl was fed into the furnace with Freedom lignite to systemically investigate its impact on mercury emissions out of the ESP. NaCl feed rate varied from 3.6 to 14.7 lb/Macf, corresponding to 1.1–4.23 lb-NaCl/ton-coal. Mercury removal efficiency across the ESP by NaCl addition alone is also plotted in Figure 9, showing NaCl significantly improved mercury capture by changing mercury chemistry in flue gas. Mercury removal increased proportionately with increased NaCl additive, from virtually no inherent mercury capture to 45.6% at 14.7 lb/Macf NaCl addition. Since both the mercury and chlorine concentrations in the ESP hopper ash were dramatically enriched while sodium and LOI concentrations were similar to the baseline test (Table 3), it is hypothesized that atomic chlorine released from NaCl decomposition in the combustion zone enhances mercury oxidation and capture on fly ash. More research is needed to further understand the detailed chemistry mechanisms.



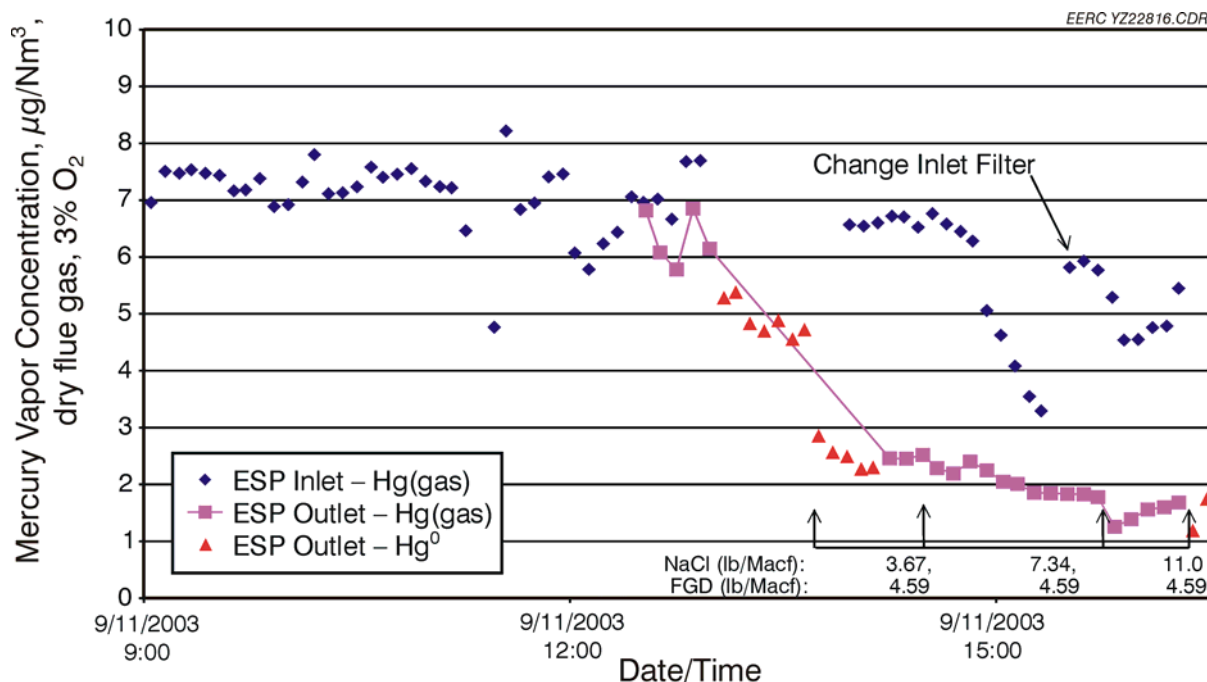


Figure 11. Mercury vapor concentrations at the ESP inlet and outlet during DARCO<sup>®</sup> FGD/NaCl injection (Freedom coal, 300°F).

Test T1-4 was performed to evaluate the integrated impact on mercury removal across the ESP while both NaCl and DARCO<sup>®</sup> FGD carbon were utilized. Figure 11 shows temporal variations in gaseous mercury concentration at the ESP inlet and outlet measured by CMMs. The mercury ESP outlet concentration was reduced from ~6.5  $\mu\text{g}/\text{Nm}^3$  at the baseline test to 2.4  $\mu\text{g}/\text{Nm}^3$  when 3.67 lb/Macf of NaCl was fed into the furnace and 4.59 lb/Macf DARCO<sup>®</sup> FGD carbon was injected upstream of the ESP. With an increased NaCl feed rate of 11 lb/Macf, the mercury emissions reduced to 1.56  $\mu\text{g}/\text{Nm}^3$ , and elemental mercury was the dominant species. It is also noted that the fly ash generated with NaCl addition caused biased CMM measurement at the ESP inlet because the fly ash filter cake formed upstream of the CMM unit adsorbed a portion of the mercury vapor. Therefore, the baseline mercury data at the ESP inlet is used for mercury removal calculations. The mercury collection efficiencies under a constant DARCO<sup>®</sup> FGD carbon injection (4.59 lb/Macf) and varied NaCl addition rates (0–14.7 lb/Macf) are plotted in Figure 9 for comparison. The 4.59 lb/Macf DARCO<sup>®</sup> FGD carbon injection had a 51.5% mercury removal. When 3.67 lb/Macf NaCl was added, the overall mercury collection efficiency increased to 67.5%, an additive response from DARCO<sup>®</sup> FGD carbon (51.5% at 4.59 lb/Macf injection alone) and NaCl (an additional 16.9% at 3.67 lb/Macf injection). The additive effect was also shown at the test of 7.34 lb/Macf NaCl (an increase of 23.7%) and 4.59 lb/Macf DARCO<sup>®</sup> FGD carbon (51.5%) with an overall mercury removal of 75%. With further increasing NaCl feed rate, however, the overall mercury removal only increased marginally to approximate 80%, indicating it may become mass transfer-limited.

Another short-term test was conducted to further confirm the additive effect of the DARCO<sup>®</sup> FGD–NaCl combination with a constant 7.34 lb/Macf NaCl and varied 0–4.59

lb/Macf DARCO<sup>®</sup> FGD carbon injection. The overall mercury removal (Figure 9) was from 23.7% at 7.34 lb/Macf NaCl injection alone to 75% at 7.34 lb/Macf NaCl plus 4.59 lb/Macf DARCO<sup>®</sup> FGD carbon injection, indicating the additive effect from DARCO<sup>®</sup> FGD–NaCl.

A 22-h test was carried out during September 17–18, 2003, to obtain long-term results on the performance of NaCl–DARCO<sup>®</sup> FGD carbon on mercury removal across the ESP. 2.57 lb/Macf DARCO<sup>®</sup> FGD carbon was injected into the ESP and 7.34 lb/Macf NaCl was fed into the furnace. The mercury emission plotted as a function of operating time in Figure 12 shows a stable value of  $\sim 3.6 \mu\text{g}/\text{Nm}^3$  during the testing period. Mercury speciation data collected with the OH method (shown in Figure 13) indicate both elemental and oxidized mercury were depleted across the ESP, having an overall mercury removal of 52.1%, which agrees with the CMM measurement result (Figure 9).

*Tests T1-5, T1-6.* Another mercury oxidant tested was SEA 2. Limited short-term tests were performed to evaluate its impact on mercury emission across the ESP as a function of injection rate (Figure 14). SEA 2 addition to the furnace significantly enhanced mercury removal, reaching 63.5% at 7.34 lb/Macf SEA 2 injection, compared to the approximately 8% inherent fly ash capture without SEA 2 addition. The efficiency curve for NaCl addition is also plotted in Figure 14 as a comparison, showing that SEA 2 was almost three time as effective as NaCl. ESP hopper ash was collected during the SEA 2 addition test for mercury, LOI, SEA 2, and sodium analyses. The analysis results (Table 4) showed a strong correlation between mercury and SEA 2 in ash, which indicates that SEA 2 species in high-temperature flue gas

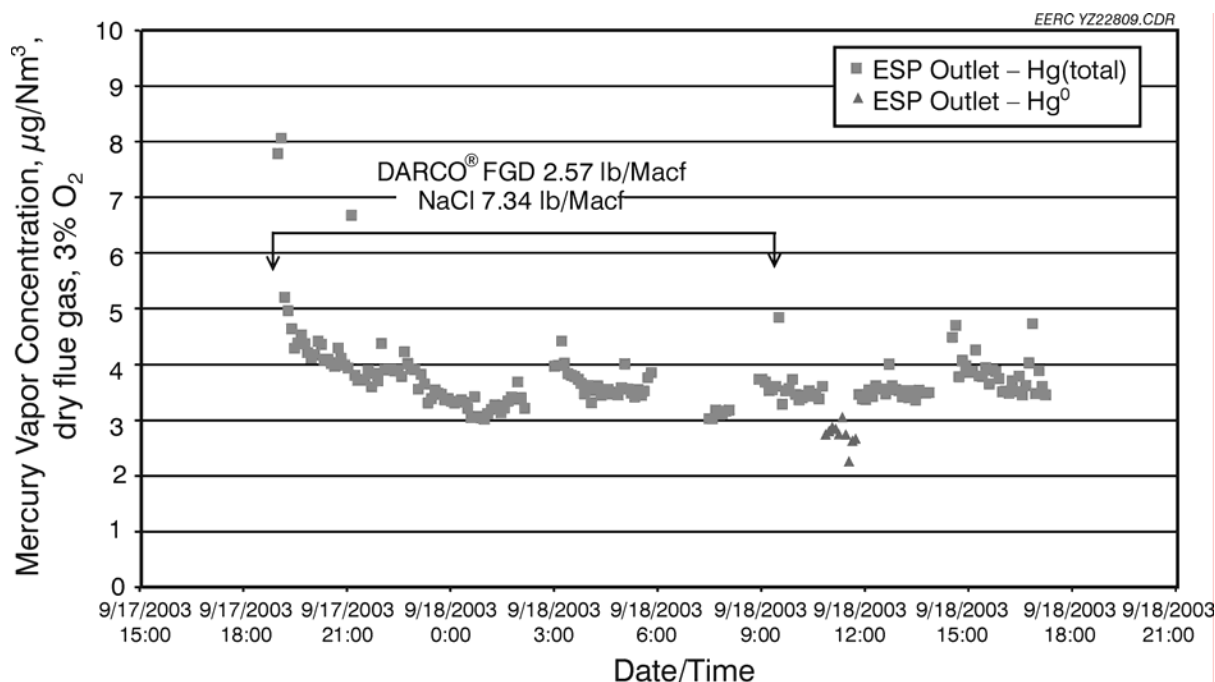


Figure 12. Mercury vapor concentrations at the ESP outlet during DARCO<sup>®</sup> FGD–NaCl injection long-term test (Freedom coal, 300°F).

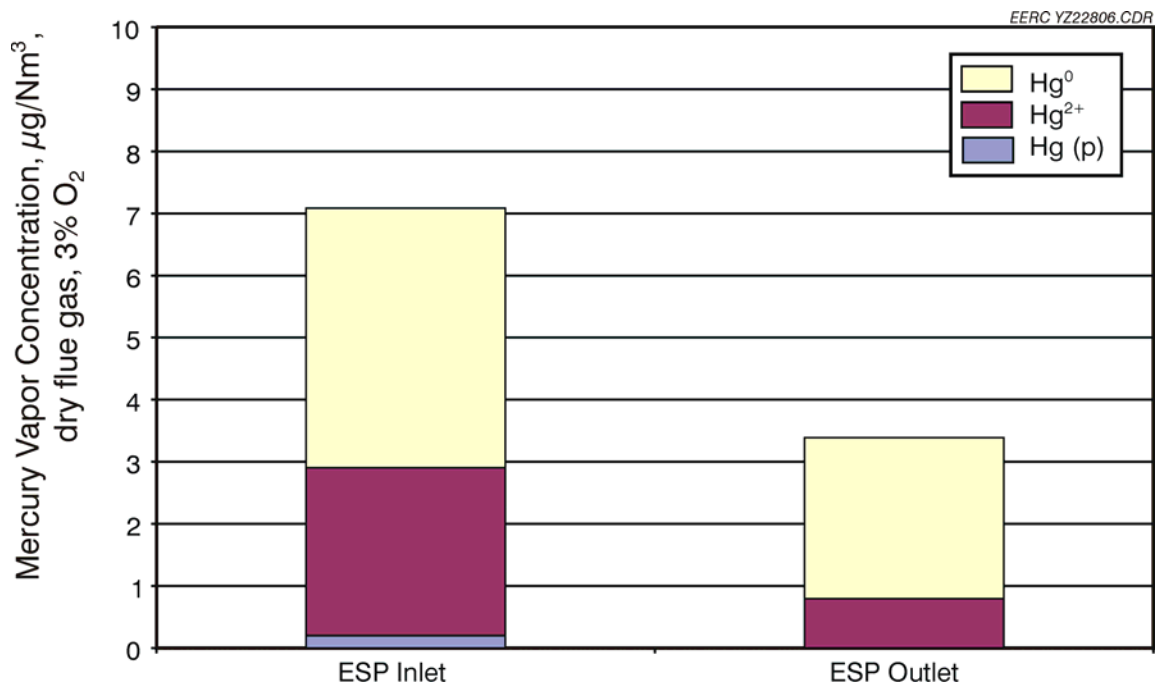


Figure 13. Mercury speciation across ESP with NaCl–DARCO<sup>®</sup> FGD carbon injection (Freedom coal, 300°F).

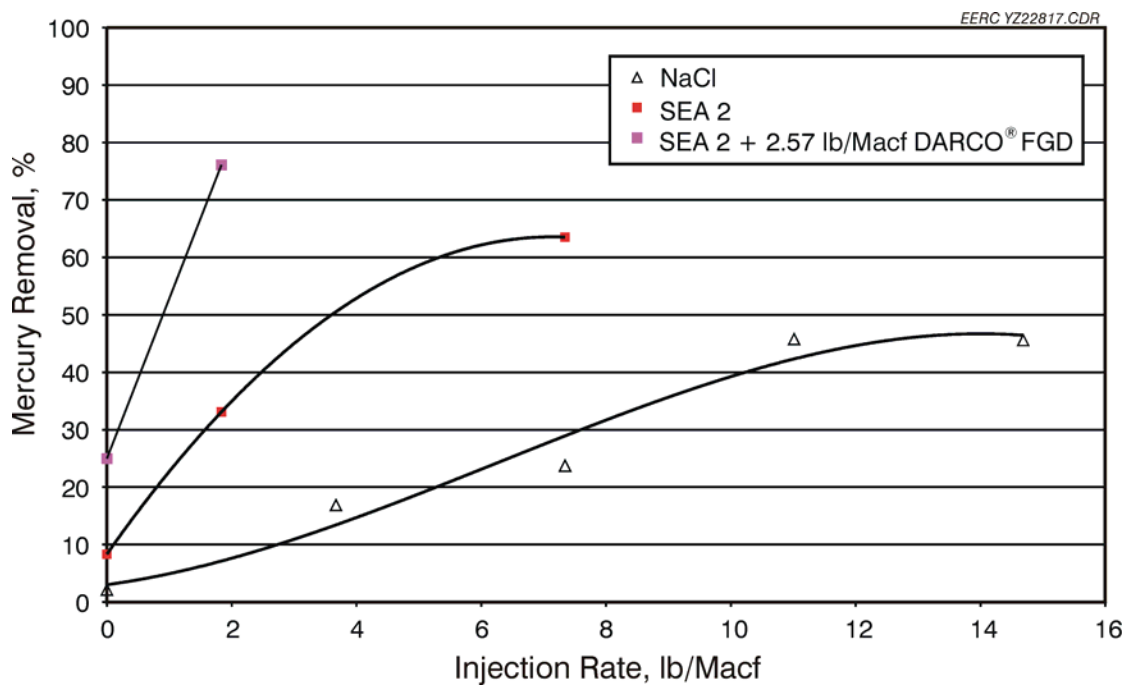


Figure 14. Effect of SEA 2 and DARCO<sup>®</sup> FGD on mercury control in the ESP.

**Table 4. ESP Hopper Ash Analysis Results – SEA 2 Injection – Task 1**

	Mercury, µg/g	LOI, %	SEA 2, µg/g	Sodium, µg/g
Baseline	0.0139	0.35	<30	11200
SEA 2 Injection	0.203	0.46	12,600	18,600

effectively convert gaseous mercury to particulate-associated mercury. Introduction of SEA 2 at 1.84 lb/Macf in combination with 2.57 lb/Macf DARCO<sup>®</sup> FGD improved mercury removal dramatically from 25% (at 2.57 lb/Macf DARCO<sup>®</sup> FGD injection) to 76.1%. The significant improvement by DARCO<sup>®</sup> FGD–SEA 2 is not merely an additive effect but more a synergistic response. The SEA 2 addition in the combustion zone not only enhances gaseous mercury conversion to particulate-associated mercury, but also improves DARCO<sup>®</sup> FGD carbon reactivity with mercury species.

*Tests T1-7 to T1-9.* The above tests have indicated that the mercury oxidants NaCl and SEA 2 benefit mercury removal by enhancing mercury reactivity with fly ash and DARCO<sup>®</sup> FGD. Therefore, the EERC developed two sorbents: an HCl-treated carbon and an EERC-treated carbon, that were tested to evaluate their effectiveness on mercury removal across the ESP. The two sorbents were injected upstream of the ESP, and the CMM data for each are plotted as a function of operating time (Figures 15 and 16). The ESP outlet mercury concentration was 7 µg/Nm<sup>3</sup> in the baseline test while the mercury concentration at the ESP inlet was around 8–9 µg/Nm<sup>3</sup> (Figure 15). With the 1.84 lb/Macf EERC-treated carbon injection rate, mercury emissions at the ESP outlet decreased to 2.4 µg/Nm<sup>3</sup>, and further decreased to 1.74 µg/Nm<sup>3</sup> at the 2.75 lb/Macf EERC-treated carbon injection rate. At the end of the EERC-treated carbon injection test, 1.84 lb/Macf SEA 2 was added to the coal feed to enhance mercury removal with a marginal decrease in mercury to 1.4 µg/Nm<sup>3</sup> at the ESP outlet. Mercury emissions with HCl-treated carbon in combination with NaCl addition are plotted in Figure 16. Mercury removal efficiencies are calculated and plotted as a function of injection rate in Figure 17. Both pre-treated sorbents show much better performance for mercury capture than the DARCO<sup>®</sup> FGD carbon. At the rate of 2.75 lb/Macf EERC-treated sorbent injection, the overall mercury removal was 76.8%, which increased to 82% when 1.84 lb/Macf SEA 2 was fed into the furnace. With the combination of NaCl- and HCl-treated sorbent injection, the mercury collection efficiency increased from 23.7% (mercury capture at the 7.34 lb/Macf NaCl injection rate) to 85.1% at 4.59 lb/Macf HCl-treated sorbent plus 7.34 lb/Macf NaCl injection. This collection efficiency was further increased to 90.5% when the NaCl injection rate increased to 11 lb/Macf.

*T1-10 to T1-13.* Short-term tests were carried out to examine the effects of other potential sorbents and oxidants on mercury removal across the ESP. Sodium tetrasulfide (Na<sub>2</sub>S<sub>4</sub>) solution was sprayed into the 300°F flue gas before it entered the ESP. Metallic zinc powder and CaCl<sub>2</sub> (aq) were added into the furnace separately. The corresponding mercury collection efficiencies are calculated based on the CMM data (Figure 18). With 11 lb/Macf CaCl<sub>2</sub> addition, the mercury removal was 44%, the same as the 11 lb/Macf NaCl injection result. Both NaCl and CaCl<sub>2</sub> injection outperformed the Na<sub>2</sub>S<sub>4</sub> and NaCl plus zinc additions. Zinc addition alone was

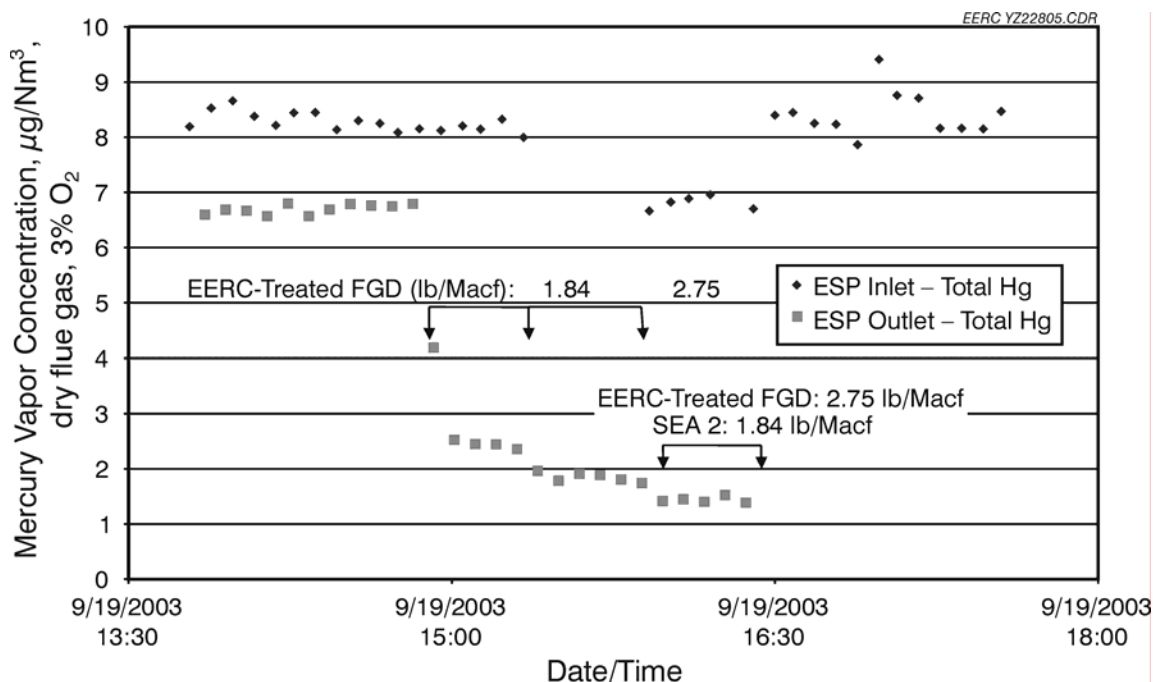


Figure 15. Mercury vapor concentrations at the ESP inlet and outlet during EERC-treated FGD carbon injection (Freedom coal, 300°F).

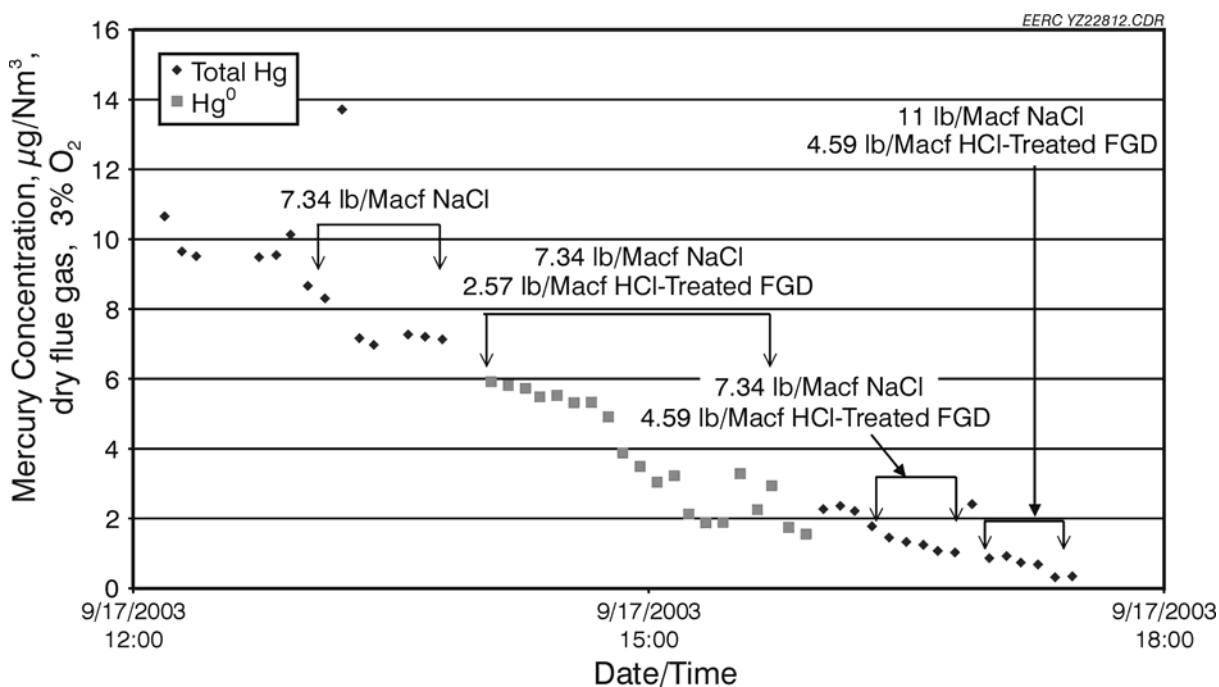


Figure 16. Mercury vapor concentration at the ESP outlet during HCl-treated FGD–NaCl injection.

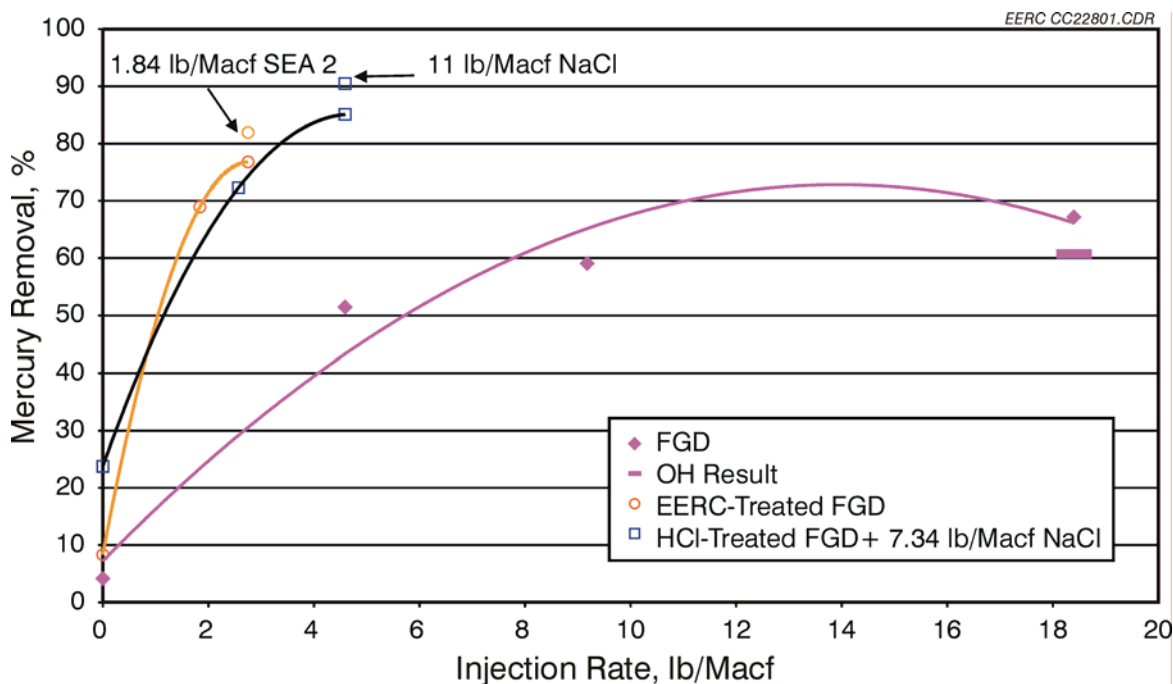


Figure 17. Mercury capture in the ESP with different sorbent injection (Freedom coal, 300°F).

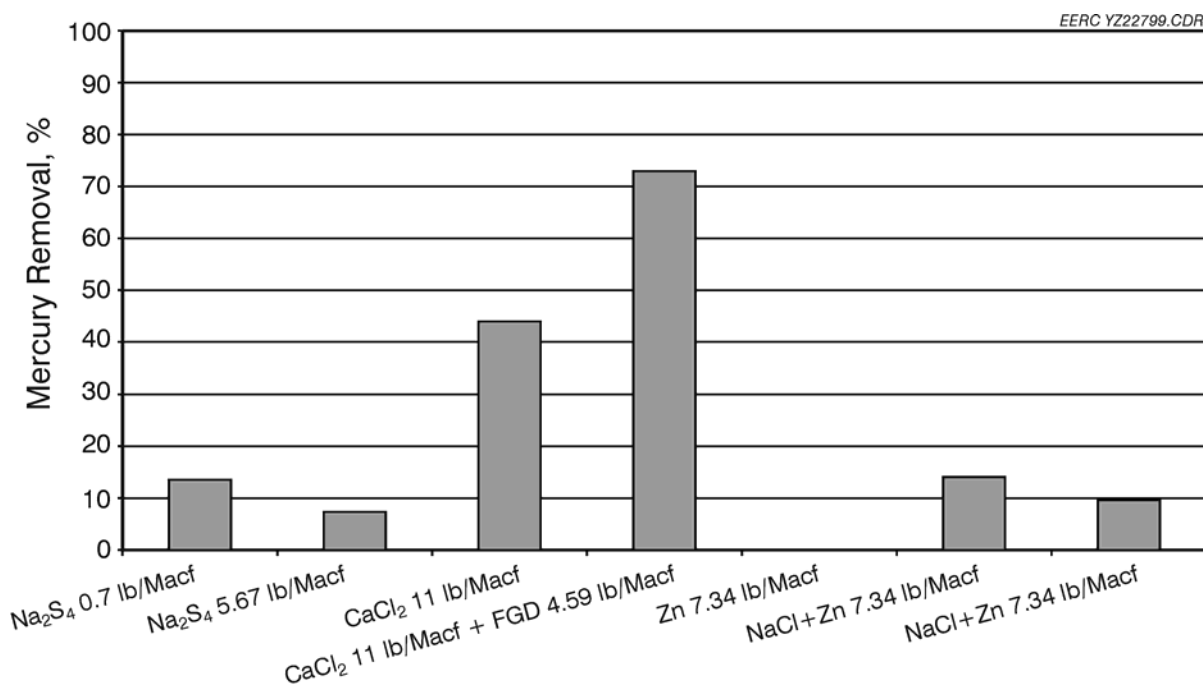


Figure 18. Effects of other additives on mercury capture in an ESP (Freedom coal, 300°F).

completely ineffective at mercury capture in the ESP. Also, metallic zinc has a negative impact on NaCl to prohibit mercury capture, probably as a result of competing reactions with the chlorine species. The combination of  $\text{CaCl}_2$  and DARCO<sup>®</sup> FGD improved mercury removal from 44% to 73%.

*Test T1-14.* ALSTOM company has developed several mercury sorbent enhancement technologies that were tested in the pilot-scale experiments. The mercury removal efficiencies of ALSTOM sorbents are plotted versus injections as shown in Figure 19. All four sorbents performed much better than the reference DARCO<sup>®</sup> FGD carbon. At a nominal 1.2 lb/Macf injection rate, the mercury removals ranged from 53% to 86%. Results of OH samples correlated well with the CMM measurement. Because of the confidential nature of ALSTOM's sorbent technology, more detail of the technology is not provided to the EERC. ALSTOM is preparing information that can be shared with the consortium related to system costs and any balance of plant impacts.

## Task 2 – Mercury Oxidation Upstream of Wet and Dry Scrubbers

As part of the effort to obtain information on possible mercury control technology options for North Dakota lignite-fired power plants, several short-term pilot-scale tests involving Tasks 2.1 and 2.2 were performed during a 4-day test period. These preliminary results were presented in the quarterly report submitted in January. Draft copies of the results of Task 2 have been submitted to the commercial sponsors for their review prior to submission as part of a DOE quarterly or final report.

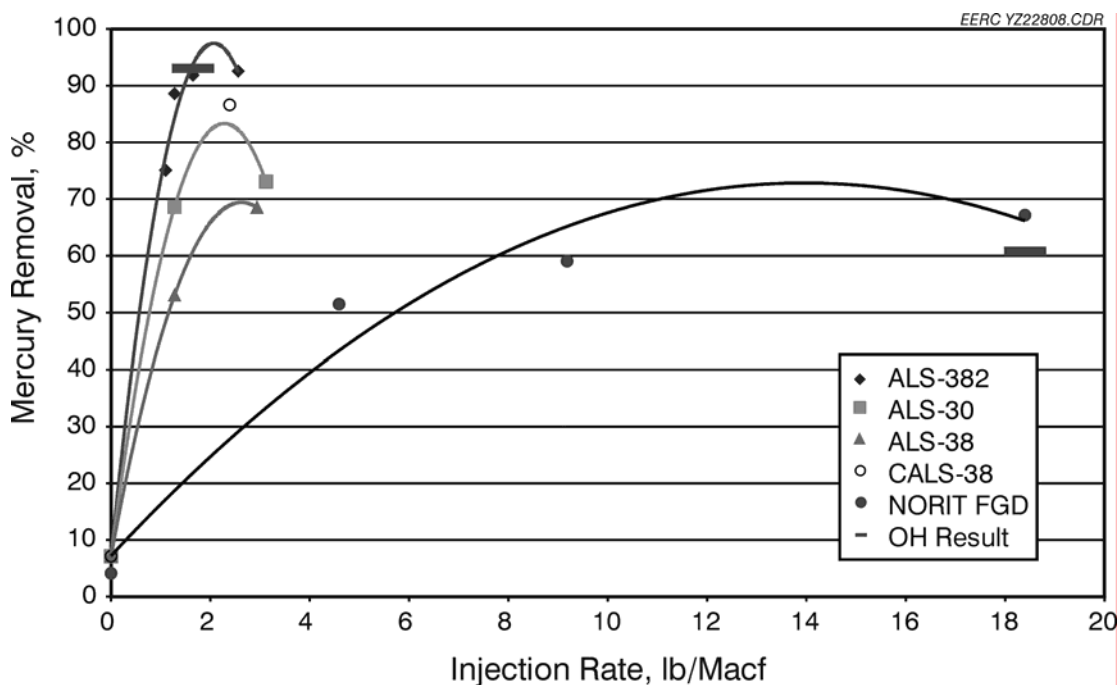


Figure 19. Mercury removal in an ESP with ALSTOM sorbent injection technologies (Freedom coal, 300°F).

### ***Task 2.1 – Elemental Mercury Oxidation Additives***

One week of short-term sorbent (Task 2.2) and furnace additive testing was accomplished in December 2003 to demonstrate mercury removal by sorbent injection combined with various oxidizing additives to simulate a scrubbed baghouse system. The 580 MJ/h (550,000 Btu/h) pulverized coal PTC unit was equipped with a Niro Inc. Production Minor Spray Dryer Model I and baghouse and fired with Center lignite coal. Table 5 summarizes the test matrix for the spray dryer–baghouse configuration. Based on previous pilot-scale testing results of ESP mercury removal effectiveness, three additives (NaCl, CaCl<sub>2</sub>, and another for which the EERC is assessing the intellectual property issues) were evaluated. CMMs were set up at the inlet to the spray dryer upstream of the sorbent injection port at the outlet of the baghouse to monitor mercury vapor concentrations continuously throughout the 4-day test. Six OH method samples were collected at the same locations to verify CMM measurements and performance of the sorbents and additive injection. A Thermo Environmental Model 15C HCl analyzer was collocated with the CMMs upstream of the spray dryer inlet to measure changes in the chloride levels of the flue gas resulting from chlorine-containing furnace additives. A preliminary review of the data indicates increased HCl content in the flue gas with increasing NaCl addition in the furnace. This is the first time, to our knowledge, that HCl and mercury concentrations have been measured simultaneously in a coal combustion flue gas. The experimental data were reduced and interpreted during this quarter. The results will be reported in an upcoming quarterly report as well as in the project final report.

**Table 5. Spray Dryer Test Sample Matrix (December 2003 run) – Task 2**

Mercury Oxidation Additive		Sorbent	
Type	Feed Rate, lb/Macf	Type	Injection Rate, lb/Macf
None	NA	None	NA
None	NA	DARCO <sup>®</sup> FGD	1.84 – 11.02
None	NA	EERC-Treated FGD	1.84 – 7.35
None	NA	Amended Silicate <sup>™</sup>	7.35
NaCl	3.67 – 11.02	None	NA
NaCl	3.67 – 11.02	DARCO <sup>®</sup> FGD	3.67
SEA 2	1.84 – 3.67	None	NA
SEA 2	1.84 – 3.67	DARCO <sup>®</sup> FGD	1.84
CaCl <sub>2</sub>	3.67 – 11.02	None	NA
CaCl <sub>2</sub>	3.67 – 11.03	DARCO <sup>®</sup> FGD	3.67

### ***Task 2.2 – Sorbent Injection***

As described in Task 2.1 and Table 5, 1 week of short-term sorbent and furnace additive testing (Task 2.1) was accomplished in December 2003. Based on previous pilot-scale testing results of ESP mercury removal effectiveness, three different sorbents (DARCO<sup>®</sup> FGD activated carbon, supplied by NORIT Americas, Inc.; an EERC-treated activated carbon; and Amended Silicate<sup>™</sup> developed by ADA Technologies, Inc.) were selected for evaluation in the PTC with a spray dryer–baghouse pollution control configuration. Preliminary results for the DARCO<sup>®</sup> FGD



sorbent injection suggest that the efficiency of the DARCO<sup>®</sup> FGD for mercury capture neared maximum when the injection rate reached 4.35 lb/Macf. At the top rate, the activated carbon sorbed nearly 57% of the mercury in the pilot-scale flue gas. The experimental data were reduced and interpreted during this quarter and will be reported in an upcoming quarterly and in the final report.

### **Task 3 – Field Tests to Determine Impacts of Oxidizing Agents on Mercury Speciation**

#### ***Task 3.1 – Impacts of Cofiring on Tire-Derived Fuels***

The activities this quarter involved delivery of the TDF to the Heskett Station and mercury measurement across the ESP with and without firing TDF. Four OH samples were taken over a period of 2 days to determine the effect TDF has on mercury speciation/removal. Chlorine levels were also measured with and without the TDF. Since the testing was completed at the end of the quarter, the data were not reduced in time for this report. Activities next quarter will involve data reduction and analysis of the TDF and coal fired during the sampling. A proximate/ultimate, Cl, and Zn analysis will be completed on both the TDF and the coal.

#### ***Task 3.2 – Impacts of Oxidation Catalysts – Coyote Station Slipstream Testing***

The oxidation catalyst testing has been put on hold. We are currently discussing intellectual property issues with the catalyst vendor.

### **Task 4 – Particulate and Mercury Control for North Dakota Lignites Using the Advanced Hybrid<sup>™</sup> Filter Technology**

The *Advanced Hybrid<sup>™</sup>* filter, which was developed by the EERC with the support of DOE and W.L. Gore & Associates Inc., combines electrostatic precipitation and fabric filtration into the same vessel. Extensive pilot-scale testing indicates that the *Advanced Hybrid<sup>™</sup>* filter provides high >99.99% particle collection efficiency with high air-to-cloth (A/C) ratios and long bag-cleaning intervals with reasonable pressure drop. The *Advanced Hybrid<sup>™</sup>* filter has unique advantages for mercury control since it provides excellent gas–solid contact in a sorbent injection application, and the gas–solid contact is expected to be further improved under a low dust-loading environment. Figure 20 shows the schematic diagram of the system. The first stage of the ESP removes approximately 90% of fly ash in the flue gas before it enters into the retrofitted *Advanced Hybrid<sup>™</sup>* filter. Selected sorbents were fed with a K-tron dual-screw feeder downstream of the ESP before the flue gas entered into the retrofitted *Advanced Hybrid<sup>™</sup>* filter. Both continuous and batch injection modes were tested as functions of the flue gas temperature (300° and 400°F) and injection rate. Mercury oxidants were fed into the furnace with the Freedom lignite. Three CMMs were used to monitor mercury vapor concentrations at the combustor outlet (Site 1) and the *Advanced Hybrid<sup>™</sup>* filter inlet (Site 2) and outlet (Site 3) continuously during the testing period. OH method sampling was also performed to verify the CMM data. OH method measurements also provide information on particle collection efficiency for the retrofitted *Advanced Hybrid<sup>™</sup>* filter.

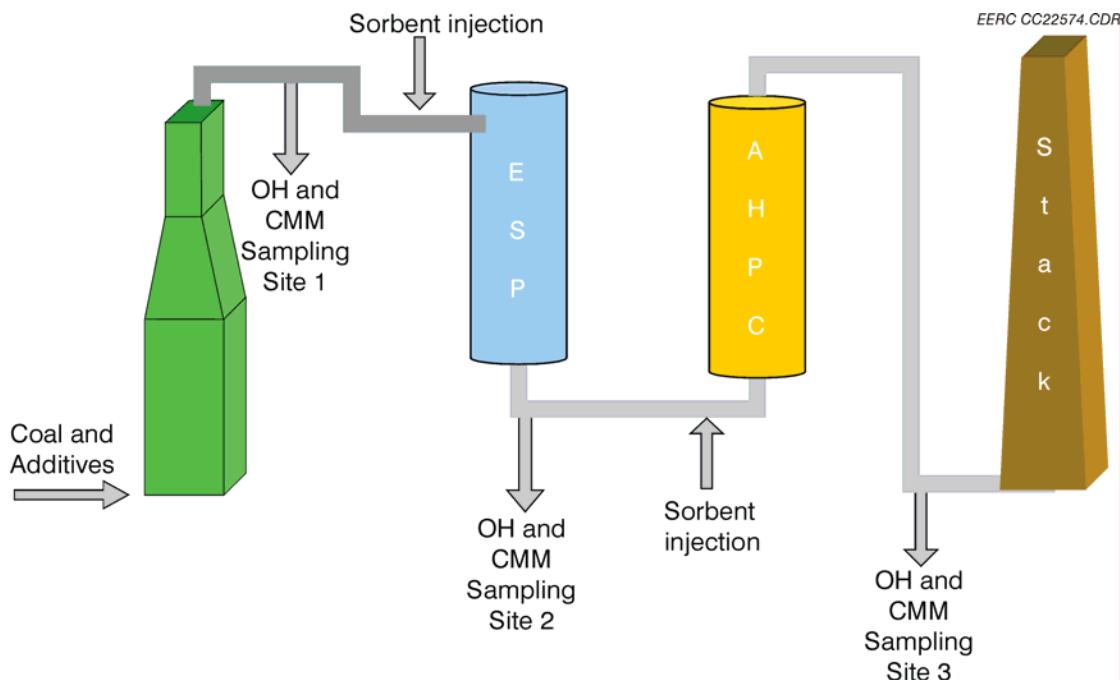


Figure 20. Injection and sampling schematic of the PTC with an ESP and *Advanced Hybrid*™ filter.

The pilot-scale test using Freedom lignite was carried out from September 8, 2003, to September 19, 2003. The ADA Amended Silicate™ sorbent was not available during the test because of a product quality problem at ADA. A summary of the test matrix for this task is listed in Table 6. DARCO® FGD and regenerated FGD were tested for mercury removal in the *Advanced Hybrid*™ filter in 300°F and 400°F flue gas with both continuous and batch injection modes. Also, mercury oxidants including NaCl, SEA 2, and zinc were examined for their impacts on mercury removal.

#### ***Advanced Hybrid*™ Filter Operation**

The first stage of the ESP was operated at 2–3-mA corona current levels to remove 90%–95% fly ash in the flue gas. The retrofitted *Advanced Hybrid*™ filter was operated under 40–60 kV with 4-mA corona current. The A/C ratio was set at 12 ft/min. Pressure drop across the filter bags started at 2.5 in. W.C. with clean bags and slowly rose because of the particle accumulation on the bag surface. Sorbent injection prior to the *Advanced Hybrid*™ filter and mercury oxidant additions into the furnace did not cause any operating difficulties in electrostatic precipitation control or bag cleanability. Particulate matter emission out of the *Advanced Hybrid*™ filter was 0–0.0002 g/scf according to the OH method dust loading measurements at the *Advanced Hybrid*™ filter outlet, indicating an extremely high particle collection efficiency >99.9% based on the 0.148–0.22 g/scf dust loading at the combustor outlet.

**Table 6. Test Matrix for Retrofitted *Advanced Hybrid*<sup>TM</sup> Filter – Task 4**

	Mercury Oxidant		Sorbent		Sorbent Injection Mode	Temperature, °F
	Category	Injection Rate, lb/Macf	Category	Injection rate, lb/Macf		
T4-1	None	NA	None	NA	NA	300
T4-2	None	NA	DARCO <sup>®</sup> FGD	0–8.08	Continuous	300
T4-3	None	NA	DARCO <sup>®</sup> FGD	0–8.08	Batch	300
T4-4	None	NA	DARCO <sup>®</sup> FGD	0–4.59	Continuous	400
T4-5	None	NA	DARCO <sup>®</sup> FGD	2.02	Batch	400
T4-6	NaCl	0–11	NA	None	NA	300
T4-7	SEA 2	0–7.34	NA	None	NA	300
T4-8	Zn/NaCl	7.34–11	NA	None	NA	300
T4-9	NaCl	3.67–7.34	DARCO <sup>®</sup> FGD	1.22–2.57	Batch/cont.	300
T4-10	None	NA	Regen.	2.2	Batch	300

Tasks 1 and 4 were commingled to produce maximum results with minimum testing days. The Freedom coal flue gas compositions and mercury levels are the same as in Task 1 and are described in Task 1.

#### ***Mercury Speciation Across the Advanced Hybrid<sup>TM</sup> Filter in Baseline Test***

*Test T4-1 (Baseline).* During the pilot-scale test, Freedom lignite with a mean mercury content of 0.05 µg/g (dry basis) was combusted at a nominal feed rate of 87 lb/hr. The coal combustion flue gas exiting the PTC was cooled down to a designated temperature of 149°C (300°F) and was then introduced into the single-wire tubular ESP unit followed by the *Advanced Hybrid*<sup>TM</sup> filter. Three CMMs were used to monitor mercury vapor concentrations at the combustor outlet and the *Advanced Hybrid*<sup>TM</sup> filter inlet and outlet. OH method samples were collected at the three locations to verify the CMM data. The purpose of the baseline test (T4-1) was to establish speciated mercury concentrations in Freedom lignite flue gas and determine whether there were changes in mercury speciation across the overall unit. CMM and OH method measurements are plotted in Figure 21, and both methods indicate most of the mercury from Freedom lignite combustion presented as elemental vapor, with 10.9%–12.9% oxidized mercury and virtually no particle-associated mercury. The total mercury concentrations at the *Advanced Hybrid*<sup>TM</sup> filter inlet and outlet are almost the same as at the combustor outlet, indicating no further mercury capture across the unit.

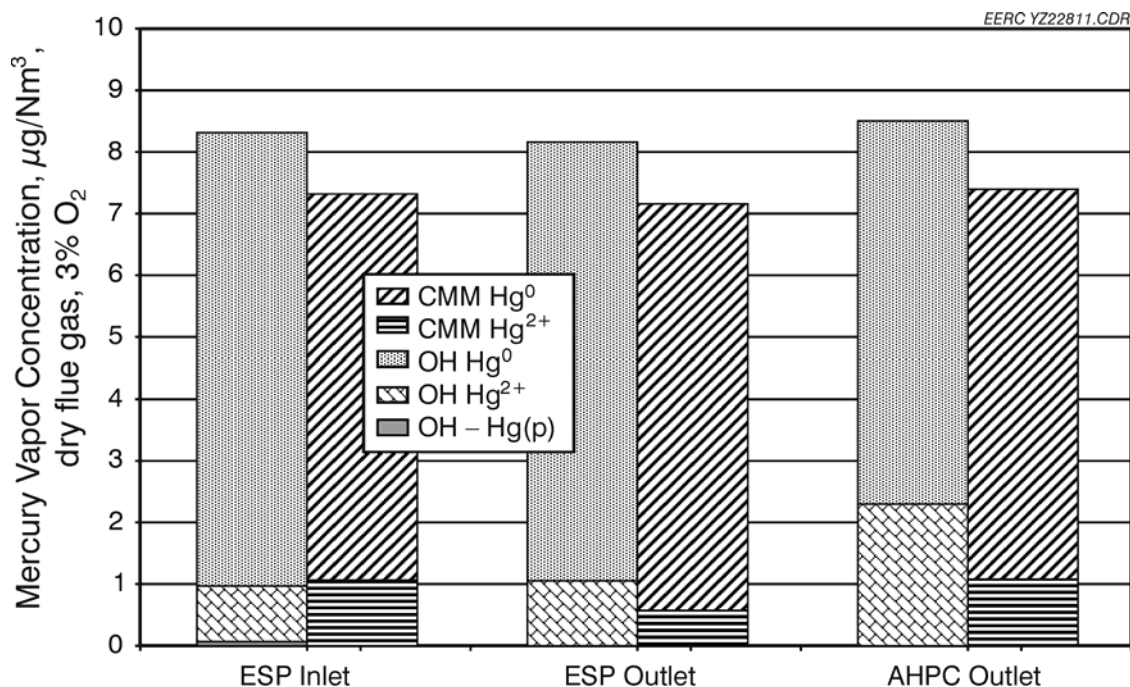


Figure 21. Mercury speciation across the ESP and *Advanced Hybrid*<sup>TM</sup> filter in Freedom coal flue gas (baseline, 300°F).

### ***Mercury Control Technology Results***

Mercury removal across the *Advanced Hybrid*<sup>TM</sup> filter was evaluated with sorbent injection, mercury oxidant addition, and combinations of sorbent and mercury oxidant. The sorbents were injected upstream of the *Advanced Hybrid*<sup>TM</sup> filter, while the mercury oxidants were added to the coal prior to introduction to the furnace. Draft copies of the results of Task 4 have been submitted to the commercial sponsors for their review prior to submission as part of a DOE quarterly or final report.

*Tests T4-2 to T4-3.* Two tests were conducted to evaluate mercury removal in the retrofit *Advanced Hybrid*<sup>TM</sup> filter with DARCO<sup>®</sup> FGD carbon as functions of injection rate and injection mode.

Figure 22 shows typical temporal variations in mercury vapor species across the system in 300°F flue gas under a continuous DARCO<sup>®</sup> FGD injection (0.92–2.02 lb/Macf) upstream of the *Advanced Hybrid*<sup>TM</sup> unit. Total mercury vapor concentrations at the combustor outlet and the *Advanced Hybrid*<sup>TM</sup> unit inlet were in the range of 5–7  $\mu\text{g}/\text{Nm}^3$  with elemental mercury dominating, indicating that no mercury conversion occurred before the contact with DARCO<sup>®</sup> FGD carbon. At the 0.92 lb/Macf DARCO<sup>®</sup> FGD injection rate, total mercury emissions out of the *Advanced Hybrid*<sup>TM</sup> filter decreased from the 6.7  $\mu\text{g}/\text{Nm}^3$  mercury emission at the baseline test to 3.5  $\mu\text{g}/\text{Nm}^3$ . At the 2.02 lb/Macf DARCO<sup>®</sup> FGD injection rate, the total mercury vapor concentration at the *Advanced Hybrid*<sup>TM</sup> filter outlet was further reduced to 2.7  $\mu\text{g}/\text{Nm}^3$  while

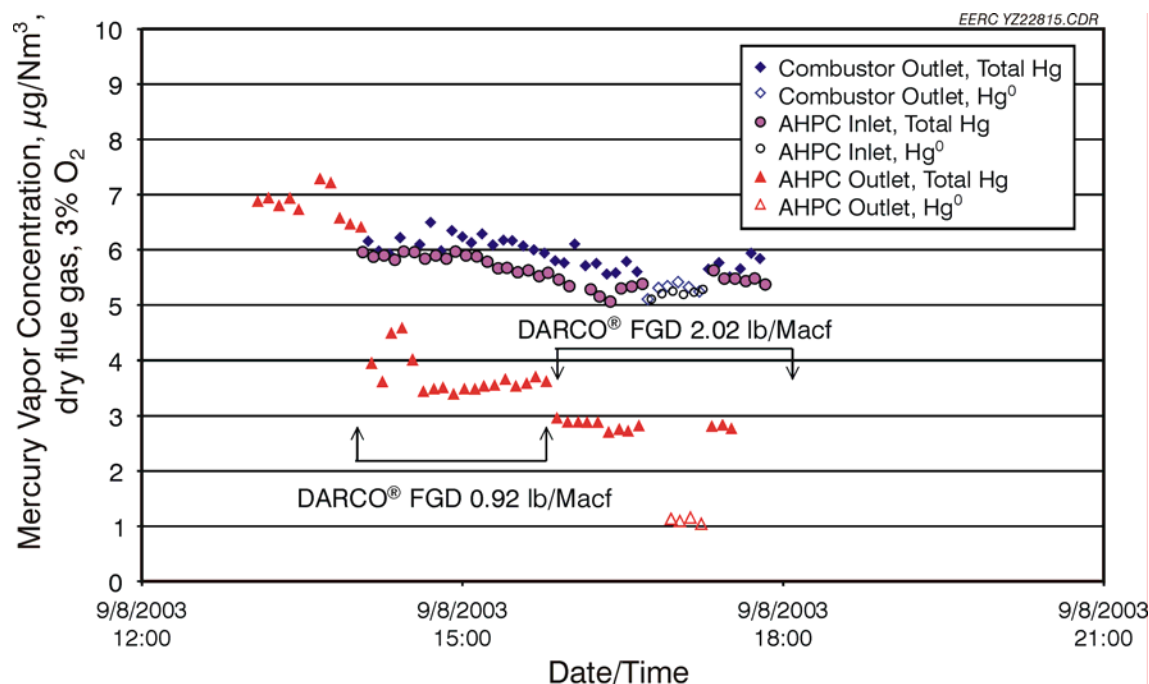


Figure 22. Mercury species across the *Advanced Hybrid™* filter with DARCO® FGD continuous injection, 300°F.

elemental mercury was only  $1.0 \mu\text{g}/\text{Nm}^3$ , indicating DARCO® FGD carbon not only captured but also oxidized mercury. OH samples were collected at the three locations (Sites 1–3) during the 2.02-lb/Macf FGD injection phase of the test. The OH results are plotted in Figure 23, showing that mercury species concentrations at the *Advanced Hybrid™* filter inlet are the same as at the combustor outlet, and reduced to  $2.4 \mu\text{g}/\text{Nm}^3$  at the *Advanced Hybrid™* filter outlet with 69.5% as oxidized mercury vapor. The CMM data agree very well with the OH measurement results. Mercury removals in the *Advanced Hybrid™* system with continuous DARCO® FGD carbon injection are calculated and plotted as a function of injection rate as shown in Figure 24.

Test T4-3 was aimed at examining the impact of sorbent batch injection on mercury removal in the retrofit *Advanced Hybrid™* filter. This was accomplished through mandatory power shutdowns to the *Advanced Hybrid™* filter while each batch of carbon was injected into the flue gas in advance of the inlet to the *Advanced Hybrid™* chamber. With the power off, all of the carbon was expected to be collected on the filter bag surface where the sorbent could capture mercury most efficiently. The entire injection period lasted less than 1 minute, and then the electric power was back online. The sorbent injection rate was determined based on the amount of the sorbent batched into the system and the time interval between the batch injections.

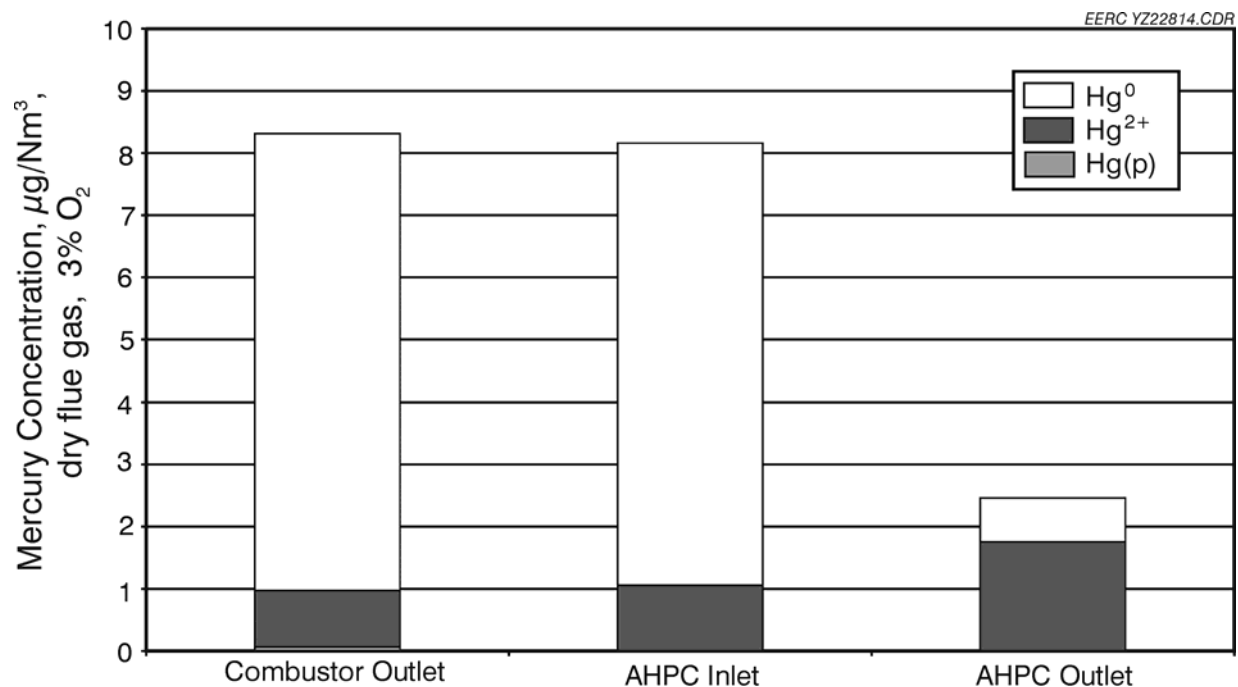


Figure 23. Mercury speciation across the retrofitted *Advanced Hybrid*<sup>™</sup> filter with 2.02 lb/Macf DARCO<sup>®</sup> FGD injection (Freedom, 300°F).

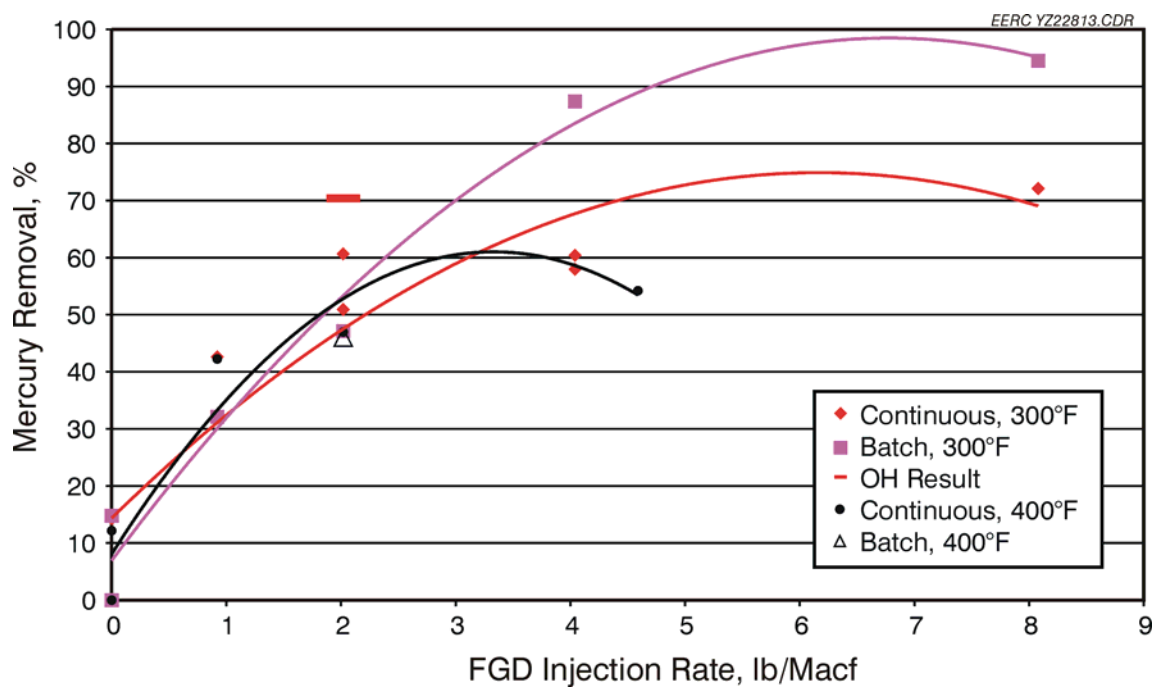


Figure 24. Mercury removal in a retrofitted *Advanced Hybrid*<sup>™</sup> filter with DARCO<sup>®</sup> FGD injection (Freedom coal).

Figure 25 shows variations in mercury emissions under batch injection mode. Before the batch injection, mercury vapor concentration at the *Advanced Hybrid*<sup>TM</sup> filter outlet was around 7.3  $\mu\text{g}/\text{Nm}^3$ , close to the 7.8  $\mu\text{g}/\text{Nm}^3$  measured at the combustor outlet, showing no inherent mercury capture across the system in the baseline test. Five grams of DARCO<sup>®</sup> FGD carbon was batched into the flue gas in a 1-h period, corresponding to a 0.92-lb/Macf sorbent injection rate. Total mercury vapor concentration was dramatically reduced to 2  $\mu\text{g}/\text{Nm}^3$  and recovered to the baseline level within a 1-h period before another 5-gram batch was added. The lowest mercury vapor concentration during the 0.92-lb/Macf batch injection test was 2  $\mu\text{g}/\text{Nm}^3$ . This indicates that the sorbent reached its capacity for mercury capture in the Freedom coal flue gas and that a higher sorbent injection rate is necessary for better mercury removal. Two 11-gram batches were then added into the system within a 1-h period to equal a 4.04-lb/Macf injection rate. The mercury emission level decreased to 0.65  $\mu\text{g}/\text{Nm}^3$  and recovered to 1.8  $\mu\text{g}/\text{Nm}^3$  after the 1-h test.

The batch test results plotted in Figure 26 show a 22-gram DARCO<sup>®</sup> FGD injection within a 2-h period, corresponding to a 2.02-lb/Macf injection rate. After the 22-gram carbon introduction into the system, the mercury emissions immediately decreased to 0.38  $\mu\text{g}/\text{Nm}^3$ , then gradually increased to 10.8  $\mu\text{g}/\text{Nm}^3$ , higher than the inlet mercury concentration. This is probably an indicator of mercury desorption from the carbon sorbent after a long exposure to the flue gas. Mercury removal efficiencies were calculated based on the inlet mercury concentrations and the time-integrated average of mercury emission and are included in Figure 24 as a function of injection rate. At the injection rate up to 2 lb/Macf, mercury capture efficiency was similar for both injection modes since the DARCO<sup>®</sup> FGD carbon reached its capacity for mercury capture

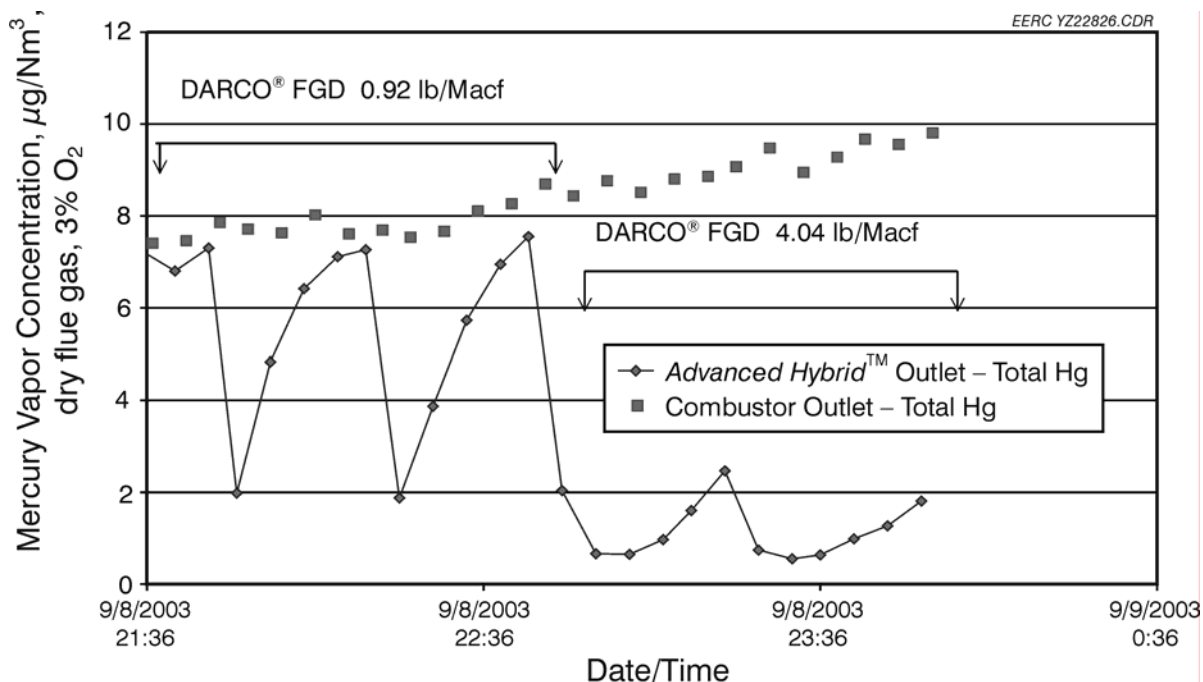


Figure 25. Mercury vapor species across the *Advanced Hybrid*<sup>TM</sup> filter under DARCO<sup>®</sup> FGD (batch injection, 300°F).

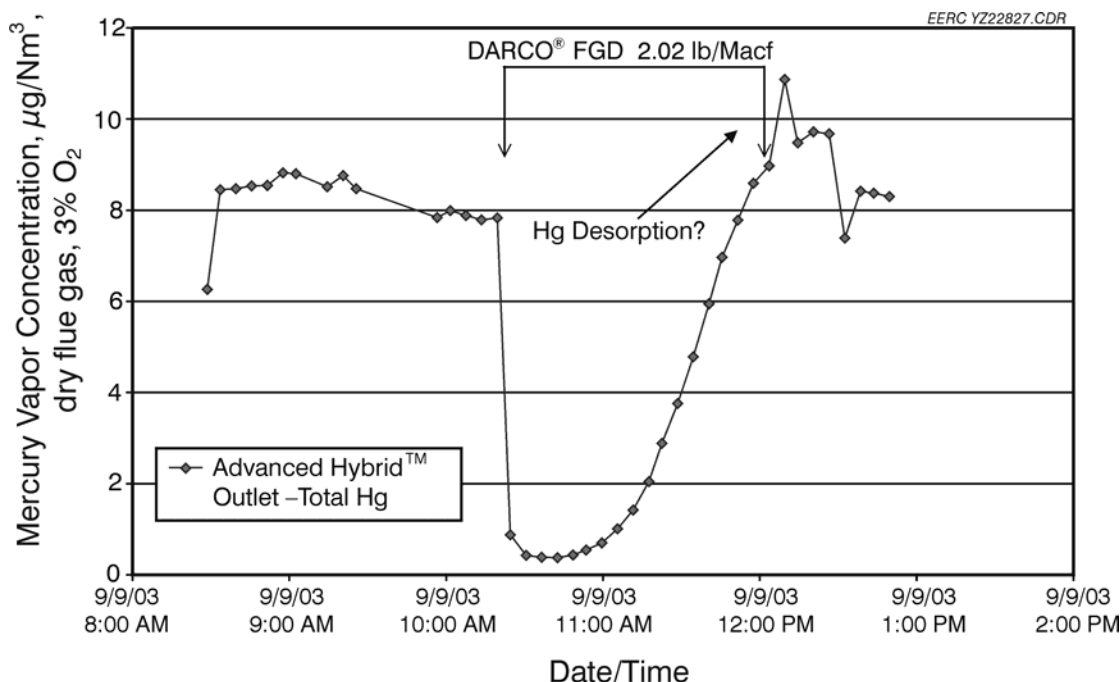


Figure 26. Mercury vapor species across the *Advanced Hybrid*™ filter under DARCO® FGD (batch injection, 300°F).

under the low injection rate. At injection rates above 4 lb/Macf, the batch mode outperformed the continuous mode (87.4% to 60.5% mercury removal, respectively) with the result that the carbon was most efficiently utilized on the filter bags' surface rather than on the collection plate. Doubling the sorbent injection rate increased the mercury removal by 7% and 12%, respectively, with the batch mode DARCO® FGD carbon injection reaching 94.5% at 8.08 lb/Macf.

*Tests T4-4 and T4-5.* Two tests were performed to evaluate mercury capture by DARCO® FGD carbon in the retrofit *Advanced Hybrid*™ filter operated at an elevated temperature of 400°F. Mercury removals by DARCO® FGD at the 400°F are plotted in Figure 24. A comparison with the 300°F testing data indicates no significant mercury removal dependence on operating temperature.

*Tests T4-6 to T4-8.* Three tests were carried out to investigate the effect of mercury oxidants, including NaCl, SEA 2, and zinc, on mercury removal in the *Advanced Hybrid*™ filter system. Figure 27 shows that with the additions of NaCl and SEA 2 to the coal prior to introduction to the furnace, mercury removal efficiencies increased significantly: 47.5% at the 11-lb/Macf NaCl injection rate and 76.7% at the 7.34-lb/Macf SEA 2 injection rate. As in Task 1, SEA 2 has a much better performance on mercury capture than NaCl in the retrofit *Advanced Hybrid*™ filter because SEA 2 (generated in the combustion zone) reacts more easily with mercury vapor and converts into particulate-associated mercury. Both the ESP and the retrofitted *Advanced Hybrid*™ filter hopper ashes were collected during the NaCl and SEA 2 injection tests and analyzed for mercury, sodium, chloride, and SEA 2 constituents. The results



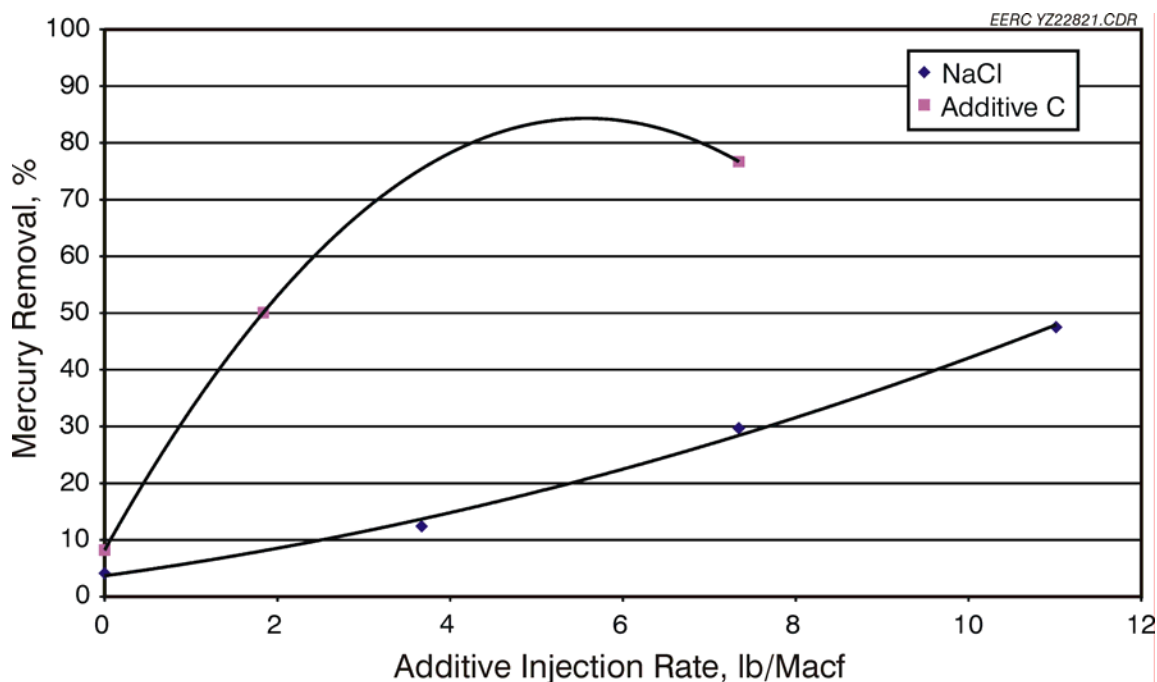


Figure 27. Effect of additives for mercury control in the *Advanced Hybrid™* filter (Freedom coal, 300°F).

are listed in Table 7. During the NaCl and SEA 2 addition tests, mercury enrichment was observed in both the ESP and *Advanced Hybrid™* hopper ashes with a higher enrichment in the finer *Advanced Hybrid™* hopper ash. Most SEA 2 constituents were present in the larger-sized ESP ash while chlorine was well distributed between the two ashes.

**Table 7. ESP and *Advanced Hybrid™* Filter Hopper Ash Analyses – Task 4**

	ESP				<i>Advanced Hybrid™</i> filter			
	Cl, μg/g	SEA 2, μg/g	Na, μg/g	Hg, μg/g	Cl, μg/g	SEA 2, μg/g	Na, μg/g	Hg, μg/g
Baseline	206	<30	11,200	0.0139	NA			
NaCl	5440	NA	18,700	0.38	2800	NA	39,500	0.614
SEA 2	NA	12,600	18,600	0.203	NA	<60	37,600	0.89

Figure 28 shows the impacts of metallic zinc and the combination of Zn and NaCl on mercury emission of the *Advanced Hybrid™* filter. The addition of zinc into the furnace alone resulted in a marginal increase of mercury capture of 13.2% at 7.34 lb/Macf. The addition of zinc and NaCl had a better mercury removal than the zinc-only addition. However, in comparison

with the results from NaCl addition, the metallic zinc had a negative impact on mercury capture since zinc will compete with mercury for the chlorine species.

*Test T4-9.* Since NaCl has shown the beneficial effect on mercury capture by enhancing reactivity between fly ash and mercury vapor. Test T4-9 was carried out to investigate mercury removal in the *Advanced Hybrid™* unit with the NaCl–DARCO® FGD carbon combination. The benefit of simultaneous injections will be a reduction in carbon usage through replacement with the more cost-effective NaCl as a mercury oxidant without causing any operating difficulty. NaCl was continuously fed into the furnace with coal while DARCO® FGD carbon was injected into the system in both continuous and batch injection modes. The data in Figure 29 show that the 3.67-lb/Macf NaCl feed rate combined with the 2.57-lb/Macf DARCO® FGD continuous injection rate resulted in 79% mercury capture, which is an additive response from separate injections of DARCO® FGD (~56% at the 2.57-lb/Macf injection rate) plus NaCl (~12.4% at the 3.67-lb/Macf injection rate). The improved 70% mercury collection efficiency matches the mercury removal at 8.08 lb/Macf DARCO® FGD without NaCl addition. Hence, the carbon injection rate was decreased to 32% by the simultaneous NaCl addition in the furnace to yield the same effect. Ontario Hydro measurements show variations of mercury species across the system caused by NaCl and DARCO® FGD additions (shown in Figure 30). More particulate-associated mercury was present in the combustor outlet sample than in the baseline test as a result of the

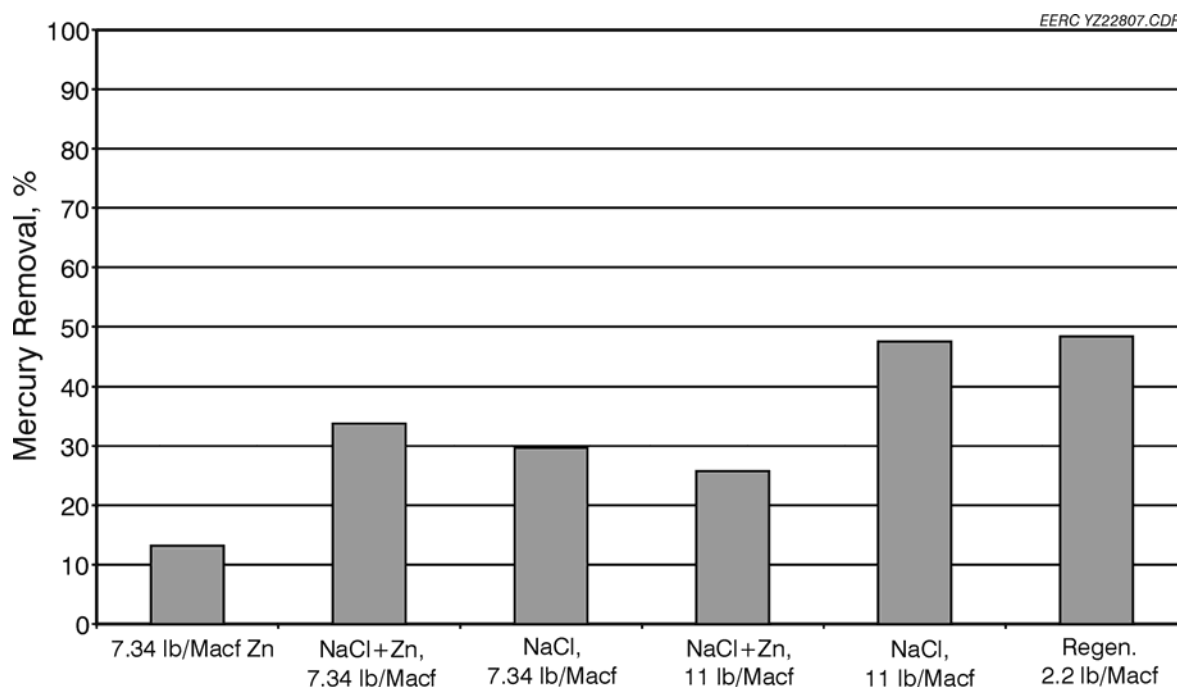


Figure 28. Effects of additives on mercury capture in a retrofitted *Advanced Hybrid™* filter (Freedom coal, 300°F).

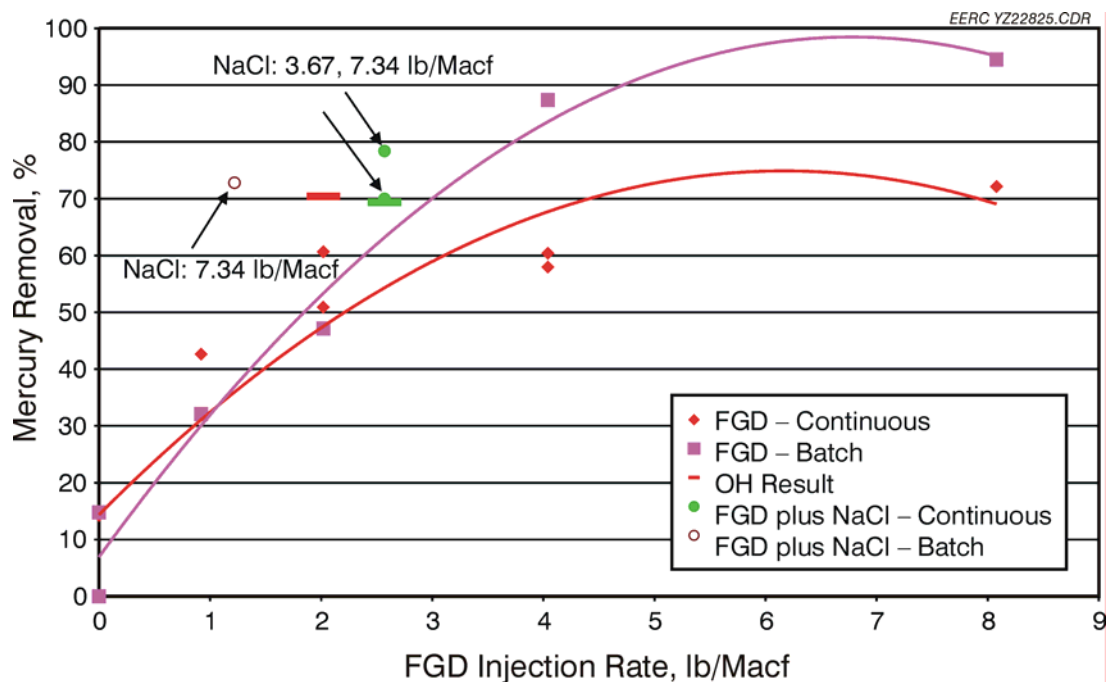


Figure 29. Mercury removal with FGD plus NaCl in the retrofitted *Advanced Hybrid*<sup>TM</sup> filter (Freedom coal, 300°F).

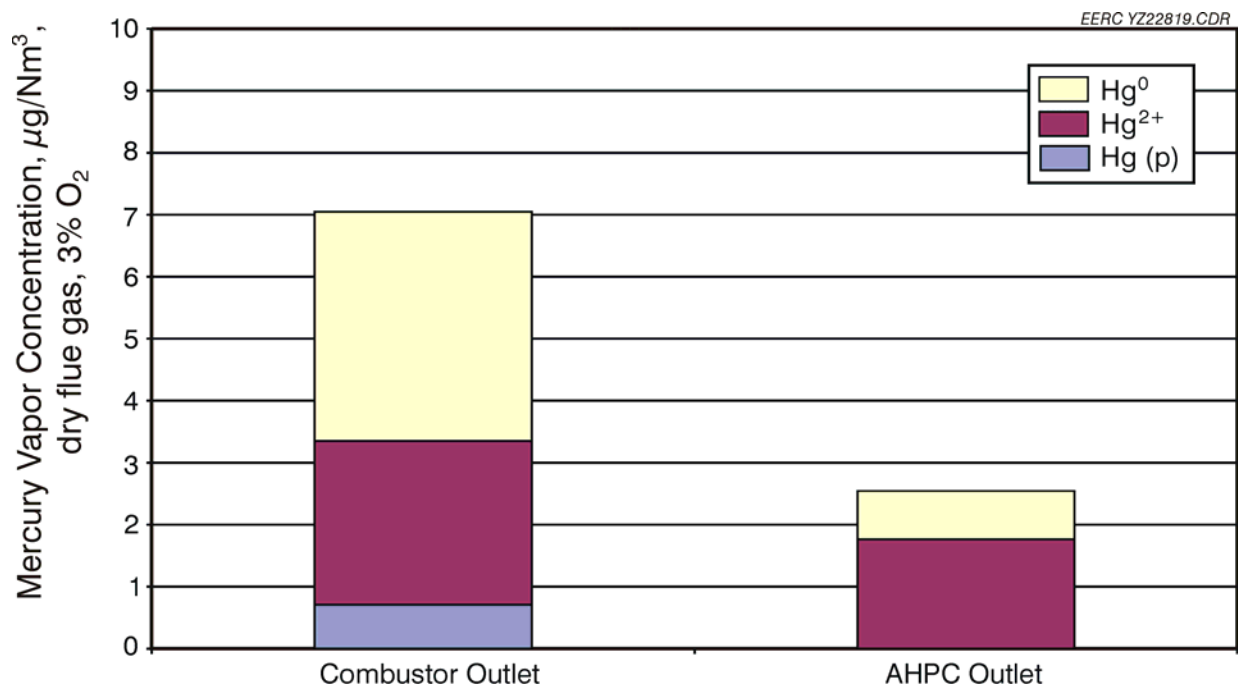


Figure 30. Mercury speciation across the retrofitted *Advanced Hybrid*<sup>TM</sup> filter with 2.57-lb/Macf DARCO<sup>®</sup> FGD plus 3.67-lb/Macf NaCl injection (Freedom coal, 300°F).

NaCl addition. The mercury removal efficiency was calculated based on the OH data, and it matches the CMM data well. Increasing the NaCl feed rate to 7.34 lb/Macf resulted in 79% mercury removal. The sum effect of NaCl and DARCO<sup>®</sup> FGD carbon was also shown in the DARCO<sup>®</sup> FGD batch injection test. With 7.34-lb/Macf NaCl and 1.22-lb/Macf DARCO<sup>®</sup> FGD added in the batch mode, the overall mercury removal reached 72.8%, of which ~39% represents the 1.22-lb/Macf DARCO<sup>®</sup> FGD batch injection and 30% represents the 7.34-lb/Macf NaCl addition.

The EERC has developed a regeneration process to reuse sorbent. Short-term Test T4-10 was performed to evaluate the effectiveness of the regenerated FGD sorbent on mercury capture in the *Advanced Hybrid*<sup>™</sup> filter. Using a 2.2-lb/Macf regenerated FGD batch injection rate, the measured mercury removal was 48% (also shown in Figure 28), almost the same as the collection efficiency achieved by DARCO<sup>®</sup> FGD carbon at the same rate. More research is needed to further explore this area.

### **Task 5 – Field Testing of Sorbents**

The construction of the trailer-mounted baghouse was completed this quarter. The unit was delivered to Basin Electric's Leland Olds Station (LOS) for sorbent injection activities. A photograph of the unit as mounted on the trailer at LOS is shown in Figure 31. The test matrix is presented in Table 8.



Figure 31. The portable baghouse unit installed at Basin Electric's Leland Olds Station for sorbent injection field tests.

**Table 8. Portable Baghouse Slipstream (Days 1 and 2) Test Matrix at Leland Olds Unit 1 – Task 5**

Mercury Oxidant		Sorbent		Baghouse Face
Category	Injection Rate, $\mu\text{g/g}^1$	Category	Injection Rate, $\text{lb/Macf (g/hr)}$	Velocity, $\text{ft/min}$
None	NA	None	NA	6
None	NA	DARCO <sup>®</sup> FGD	1.9 (70)	6
None	NA	DARCO <sup>®</sup> FGD	2 (100)	8
None	NA	DARCO <sup>®</sup> FGD	2 (124)	10
Chlorine	500	DARCO <sup>®</sup> FGD	0.9 (34)	6
Chlorine	500	DARCO <sup>®</sup> FGD	1 (50)	8
Chlorine	300	DARCO <sup>®</sup> FGD	2 (100)	8

<sup>1</sup>Chlorine added to make the  $\mu\text{g/g}$  equivalent in the coal

Sorbent injection activities using the EERC trailer-mounted sorbent injection system took place for 1 week at the end of the quarter. DARCO<sup>®</sup> FGD was injected at various rates at the inlet to the trailer-mounted baghouse. During the weeklong test, A/C ratios were varied to achieve face velocities between 6 and 10 ft/min to investigate the effect of face velocity on mercury control. Sorbent injection is performed using a self-contained feed system, injecting sorbent into the 8-in. header at the entrance to the baghouse at rates ranging from 2 to 10 lb/MMft<sup>3</sup>, depending on the level of mercury reduced.

Sorbent injection is performed using a self-contained feed system, injecting sorbent into the 8-in. header at the entrance to the baghouse at a nominal rate of 2–10 lb/MMft<sup>3</sup>, depending on the level of mercury reduced. Mercury measurement in the flue gas is determined by CMMs installed at the ESP inlet and baghouse outlet and limited OH sampling at the baghouse inlet and outlet. Standard quality assurance/quality control (QA/QC) practices are followed for all mercury-sampling activities. A field spike and blank are taken during each OH sampling period.

Data from the April 1 and 2 tests only is included in this report. Table 9 contains the information for the tests conducted on April 1 and 2, 2004. Preliminary analysis of the data indicated that the maximum mercury removal achieved with the baghouse was with 300 ppm Cl (coal equivalent) and 2 lb/Macf of activated carbon injection. The data collected on April 2 showed residual effects from injecting Cl in the system the previous day. Figure 32 shows the effect face velocity has on mercury removal in a baghouse. The outlet mercury concentration dropped as the face velocity was increased from 6 to 8 ft/min and finally to 10 ft/min.

Results from the remaining tests will be reduced, compiled, interpreted, and reported in an upcoming quarterly report. Additional data will also be collected to determine the true effect residual Cl has on mercury removal.

**Table 9. Preliminary Data from Leland Olds Baghouse Sampling – Task 5**

Run Conditions		Day 1			Day 2	
Face Velocity, ft/min	6	7.93	7.86	5.9	7.9	10.0
BH Flow, acfm	1342	1794	1777	1340	1793	2265
Chlorine (coal equivalent), ppm	500	500	300	0	0	0
Carbon, g/hr	34.28	49.93	99.86	69.4	98.31	124
lb/Macf	0.9282	1.014	2.06	1.90	2.01	2.01
Hg, ESP inlet, $\mu\text{g}/\text{m}^3$ *	9.0	8.4	8.8	9.6	9.5	9.5
O <sub>2</sub> , average	3.9	3.9	3.9	3.9	3.9	4.0
Hg, BH outlet, $\mu\text{g}/\text{m}^3$ *	3.0	2.76	1.27	2.9	2.1	2.1
O <sub>2</sub> , average	5.25	5.25	5.30	6.0	6.0	6.0
Average Reduction, %	67	67	86	70	78	78

\* Corrected to 3% O<sub>2</sub>.

## FUTURE WORK – NEXT QUARTER

Work in the upcoming quarter will involve data reduction and interpretation of existing field data related to the portable baghouse test runs, continued field testing using the portable baghouse unit at Leland Olds, and preparations for additional field testing. Specifically:

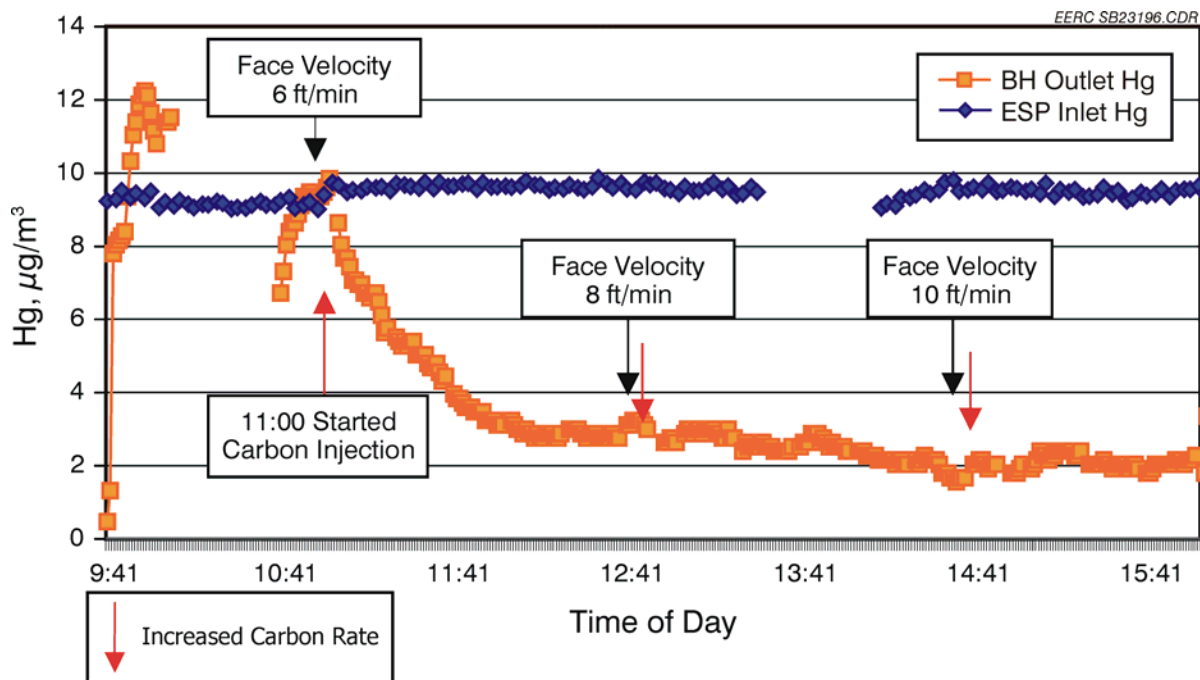


Figure 32. Mercury levels in the flue gas on Day 2, with increasing carbon injection rate to maintain a 2-lb/Macf carbon injection rate in the baghouse while increasing the A/C ratio (face velocity).

- The results from test runs performed under Task 2 will be distributed to the project's commercial sponsors for review and comments. Once comments are received and addressed, the results will be released to DOE.
- Field tests for Task 3 are expected to begin in the second quarter of 2004.
- Field tests under Task 5 will continue at Leland Olds Station using the baghouse and auxiliary equipment on the trailer bed. Data reduction and analysis will begin.

The project's milestone chart is presented in Figure 33.

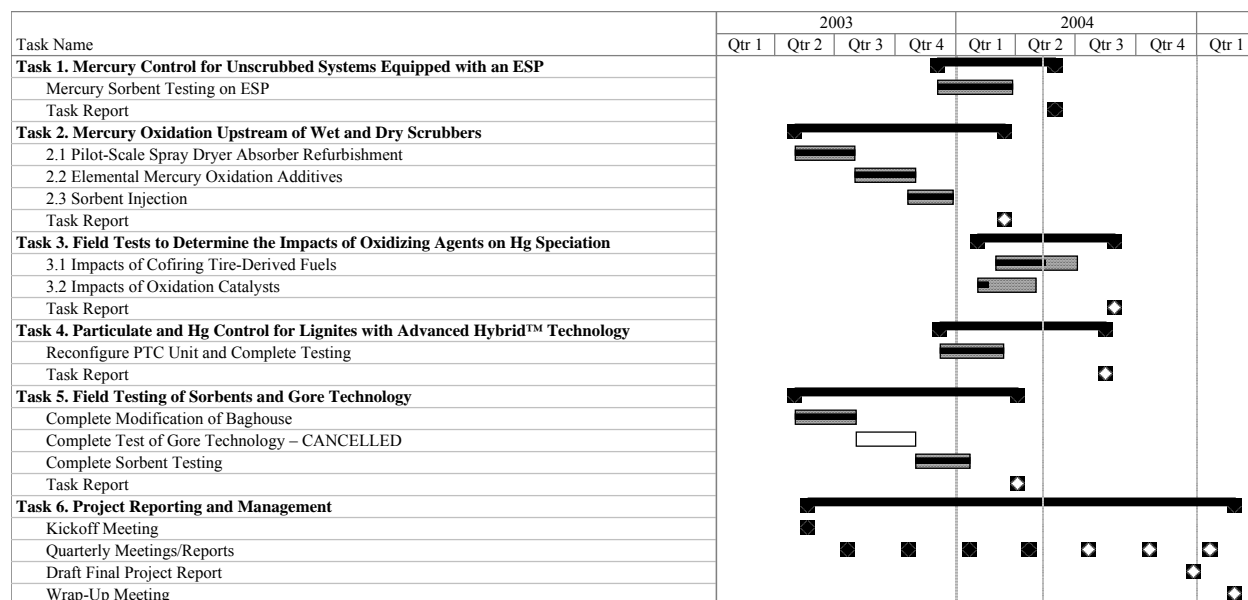


Figure 33. Milestone chart.

## REFERENCES

1. Pavlish, J.H.; Holmes, M.J.; Benson, S.B.; Crocker, C.R.; Galbreath, K.C. Application of Sorbents for Mercury Control for Utilities Burning Lignite Coal. *Fuel Process. Technol.* **2004**, *85*, 563–576.
2. Chang, R.; Strohfus, M. *The Evaluation of Chemical Additives for Mercury Emission Control at Great River Energy*; Final Report to the North Dakota Industrial Commission; Jan 2003.
3. Felsvang, K.; Gleiser, R.; Juip, G.; Nielsen, K.K. Activated Carbon Injection in Spray Dryer/ESP/FF for Mercury and Toxics Control. *Fuel Process. Technol.* **1994**, *39*, 417–430.

4. Pavlish, J.H.; Sondreal, E.A.; Mann, M.D.; Olson, E.S.; Galbreath, K.C.; Laudal, D.L.; Benson, S.A. Status Review of Mercury Control Options for Coal-Fired Power Plants. *Fuel Process. Technol.*, **2003**, 82, (2–3), 89–165.
5. Carey, T.R.; Hargrove, O.W.; Richardson, C.F.; Chang, R.; Meserole, F.B. Factors Affecting Mercury Control in Utility Flue Gas Using Activated Carbon. *J. Air Waste Manage. Assoc.* **1998**, 48, 1166–1174.
6. Dunham, G.E.; Olson, E.S.; Miller, S.J. Impact of Flue Gas Constituents on Carbon Sorbents. In *Proceedings of the Air Quality II: Mercury, Trace Elements, and Particulate Matter Conference*; McLean, VA, Sept 19–21, 2000; Paper A4-3.
7. Olson, E.S.; Sharma, R.K.; Miller, S.J.; Dunham, G.E. Identification of the Breakthrough Oxidized Mercury Species from Sorbents in Flue Gas. In *Proceedings of the Specialty Conference on Mercury in the Environment*; Minneapolis, MN, Sept 15–17, 1999; pp 121–126.
8. Bustard, J.; Durham, M.; Starns, T.; Lindsey, C.; Martin, C.; Schlager, R.; Bladrey, K. Full-Scale Evaluation of Sorbent Injection for Mercury Control on Coal-Fired Power Plants. In *Proceedings of Air Quality III, Mercury, Trace Elements, and Particulate Matter Conference*; Arlington, VA, Sept 10–12, 2002; Energy & Environmental Research Center: Grand Forks, ND, 2002.
9. Sjostrom, S.; Richardson, C.; Chang, R. *Evaluation of Mercury Emissions and Control Options for Great River Energy*; Final Report for North Dakota Industrial Commission, June 2001.
10. Liu, W.; Vidic, R.D.; Brown, T.D. Optimization of Sulfur Impregnation Protocol for Fixed-Bed Application of Activated Carbon-Based Sorbents for Gas-Phase Mercury Removal. *Environ. Sci. Technol.* **1998**, 32, 531–538.
11. Ghorishi, S.B.; Kenney, R.M.; Serre, S.D.; Gullett, B.K.; Jozewicz, W.S. Development of a Cl-Impregnated Carbon for Entrained-Flow Capture of Elemental Mercury. *Environ. Sci. Technol.* **2002**, 36, 4454–4459.
12. Dunham, G.E.; Miller, S.J.; Laudal, D.L. *Investigation of Sorbent Injection for Mercury Control in Coal-Fired Boilers*; Final Report for EPRI and DOE; Energy & Environmental Research Center: Grand Forks, ND, Sept 1998.
13. Laumb, J.D.; Benson, S.A.; Olson, E.S. X-Ray Photoelectron Spectroscopy Analysis of Mercury Sorbent Surface Chemistry. *Air Quality III: Mercury, Trace Elements, and Particulate Matter*, Special Issue of *Fuel Process. Technol.* **2004**, 85 (6–7), 577–585.
14. Benson, S.A.; Olson, E.S.; Crocker, C.R.; Pavlish, J.H.; Holmes, M.J. Mercury Sorbent Testing in Simulated Low-Rank Coal Flue Gases. In *Proceedings of the 6th Electric Utilities Environmental Conference*; Jan 27–30, 2003.



15. Lovell, J.; Butz, J.; Broderick, T. Ultimate Fate of Mercury Sorbents. In *Proceedings of the Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference*; Arlington, VA, Sept 9–12, 2002; Energy & Environmental Research Center: Grand Forks, ND, 2002.
16. Laudal, D.L.; Thompson, J.S.; Pavlish, J.H. Brickett, L.A.; Chu, P. Use of Continuous Mercury Monitors at Coal-Fired Utilities. *Air Quality III: Mercury, Trace Elements, and Particulate Matter*, Special Issue of *Fuel Process. Technol.* **2004**, 85 (6–7), 501–511.
17. Galbreath, K.C.; Zygarlicke, C.J.; Mercury Transformations in Coal Combustion Flue Gas. In *Air Quality: Mercury, Trace Elements, and Particulate Matter*, Special Issue of *Fuel Process. Technol.* **2000**, 65–66, 289–310.
18. Miller, S.J.; Zhuang, Y.; Olderbak, M.R. *Mercury Control with the Advanced Hybrid Particulate Collector*. Technical Progress Report; Energy & Environmental Research Center: Grand Forks, ND, Nov 2002.
19. Pavlish, J.H.; Holmes, M.J.; Benson, S.A.; Crocker, C.R.; Olson, E.S.; Galbreath, K.C.; Zhuang, Y.; Pavlish, B.M. *Mercury Control Technologies for Electric Utilities Burning Lignite Coal*. Draft Final Report [Feb 1, 2002 – March 31, 2003] for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-98FT40321; Energy & Environmental Research Center: Grand Forks, ND, April 2003.